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VANADIUM 8-HYDROXYQUINOLATE AS A REAGENT FOR THE DETECTION OF ALCOHOLS, THIOLS AND AMINES

by

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The black complex of 8-hydroxyquinoline with vanadate ("vanadium 8-hydroxyquinolate", $(C_9H_6ON)_2VO.OH$) is known[1] to be slightly soluble in pure benzene and chloroform to give almost black solutions, but in commercial chloroform a bright red solution results. The difference has been ascribed[2] to the presence of alcohol in the commercial chloroform, and the colour change has been employed, in aqueous media, as a qualitative test for alcohols[3]. A mechanism for the reaction has been proposed, and the pure chloroform solution used as a test for some alcohols by BIELIG AND BAYER[4]. The present paper examines the reactions of most types of alcohols, and, indeed, of most classes of organic compounds, with vanadium 8-hydroxyquinolate and extends its usefulness as an organic analytical reagent. The authors propose to publish separately further observations on the mechanisms of the reactions involved.

The complex was found to be more soluble in tetrachloro-ethane and *o*-dichlorobenzene (solutions up to 1% have been prepared) than in chloroform, giving solutions that were shown by chromatography on alumina to contain one species only, but only sparingly soluble in trichloroethylene, tetrachloroethylene and pentachloroethane. The action of heat on a commercial tetrachloroethane solution leads to the formation of a blue colour that is known[4] to be due to the formation of an inner-complex salt of the formula $[(C_9H_6ON)_2.V(OH)_2]Cl$ with the hydrogen chloride that arises from hydrolysis of the solvent by small quantities of moisture that are normally present. A rigourously dried solvent does not cause this colour change, unless the reagent solution is exposed to light for a long period, when the photochemically produced hydrogen chloride again forms the blue solution. Similar reactions with organic compounds are obtained with the black and blue forms, but the blue variety was found to be less sensitive than the black.

EXPERIMENTAL

Reagents

1. *Vanadium 8-hydroxyquinolate*[5]. To a hot, weakly acid solution of ammonium vanadate, buffered with ammonium acetate (pH 3 to 6), add a 2% solution of AR 8-hydroxyquinoline in 5% acetic acid until precipitation is complete. Collect the black precipitate on a sintered-glass filter, wash with hot water and dry at 120° C. Purify by boiling the finely crushed product with benzene to remove co-precipitated 8-hydroxyquinoline, filter, wash with hot benzene and dry at 120° C.
2. *Tetrachloroethane*. Dry B.D.H. technical tetrachloroethane over freshly ignited lime.

3. *o-Dichlorobenzene.* Distil B.D.H. technical *o*-dichlorobenzene. Reject the first 5% and collect the fraction of boiling point 180-182° C. (By means of the reagent the presence of alcoholic hydroxyl groups may be demonstrated in some specimens of technical *o*-dichlorobenzene).

4. *Reagent solution.* Dissolve 18-19 mg of vanadium 8-hydroxyquinolate in 250 ml of dry tetrachloroethane by warming to 70-80° C. The resulting solution is approximately $2 \cdot 10^{-4} M$.

The reagent solution may also be prepared rapidly and directly from ammonium vanadate and 8-hydroxyquinoline as follows: dissolve 50 mg of AR 8-hydroxyquinoline in 100 ml of tetrachloroethane or *o*-dichlorobenzene, and add approximately 50 mg of AR ammonium vanadate. Maintain the mixture at 130° C for half an hour, cool and filter. Dilute, if necessary, to give a solution of the same colour intensity as the reagent prepared from the solid. The reagent prepared in this way is not so sensitive to small quantities of alcohols because the excess of 8-hydroxyquinoline inhibits the colour change from black to red.

Reactions of the tetrachloroethane solution

Procedure. To 1-2 ml of the reagent solution add 2-3 drops, or about 0.1 g of the compound to be tested, (this corresponds to a molecular ratio of 5000 : 1 for a molecular weight of 100). If no colour change occurs in 10-15 minutes, warm gently and examine the solution after it has cooled to room temperature.

The following table summarizes the results obtained:

COMPOUND	REACTION
1. *Simple alcohols*	
Methanol[3,4], ethanol[3,4], *iso*-propanol[3,4], n-[3], *sec*-, *tert*-butanol, *n*-pentanol[3], decyl alcohol, tri-*n*-amyl carbinol, cetyl alcohol, 2 : 4-dihydroxy-2-methyl pentane, 2-hydroxyethyl methyl ether, glycerine[3], diacetone alcohol[3], allyl alcohol, cyclohexanol[3], benzyl alcohol.	Black to permanent red in the cold. The *tert*-alcohols react much more slowly than the others. (The colour with benzyl alcohol slowly fades to yellow.)
2. *Other alcohols*	
Pentaerythritol, triphenyl carbinol.	Black to dark purple on warming.
Higher polyhydric alcohols (mannitol, sorbitol), simple sugars and sugars with two or three blocked hydroxyl groups.	No change.
3. *Thiols*	
Ethyl, benzyl, *p*-nitrobenzyl and *tert*-butyl mercaptans.	Black to bright green in the cold. Turned lemon-yellow by a large excess. (Except *tert*-butyl.)
Thiophenol.	Black to green to deep yellow in the cold.
4. *Amines*	
(a) Aliphatic.	
n-butylamine, tetradecylamine.	Black to light golden yellow in the cold.
Triethylamine.	Black to light green in the cold.
(b) Aromatic.	
Aniline.	Black to dark green in the cold.
Methyl aniline.	No rapid change, hot or cold, black to deep orange-yellow overnight.
Dimethyl aniline.	No rapid change, hot or cold, black to dark green in two days.
Pyridine.	Black to yellow on warming.
Diphenylamine.	No change.
5. *Peroxides*	
Dibenzoyl peroxide.	No change.

tert-butyl hydroperoxide.	Grey emulsion in the cold, going brown in an hour and finally yellow. On heating, grey to yellow *via* a fleeting red.
tert-butyl hydroperoxide + ethanol.	Black to red (normal alcohol reaction), then fading to yellow in two hours.
6. *Carboxylic acids and phenols*	
Acetic acid[4], phenol[3], phloroglucinol.	Black to blue in the cold.
Trichloroacetic acid.	Immediate black to blue, green with excess.
Caproic, stearic and mucic acids.	No change.
Thioacetic acid ($CH_3.CO.SH$).	Black to blue to dark green to light green in the cold.
7. *Polyfunctional compounds*	
2-Mercaptoethanol.	Black to orange-yellow in the cold.
Diethylethanolamine, ethanolamine.	Black to red instantaneously, soon fading to yellow.
Amino-acids.	No change.
Thio-urea.	Black to dark green on warming.
Phenyl thio-urea.	Black to green overnight.
1:3-Dimercapto-2-hydroxypropane.	Black to green to yellow in the cold.
1:2-Dimercapto-3-hydroxypropane.	Black to red to yellow-brown in the cold, slowly fading to yellow.
Thioglycollic acid.	Decolorized in the cold.
8. *Keto-Enol tautomers*	
Diethyl malonate, ethyl acetoacetate, 1:4:4-tricarbethoxy-1-en-3-one.	No change. (Commercial acetoacetic ester contains ethanol and gives the usual alcohol reaction).
9. *Miscellaneous compounds*	
Dicyclohexylidene glucose.	Black to dark purple on warming.
DL-Penicillamine hydrochloride.	Black to blue in the cold.
Methyl ester of the above.	Black to blue in the cold, going green on warming.
N-(3:4:6-triacetyl D-glucosyl)-piperidene, 2-phenyl-3-thio-4:6-dimethyl-5-keto-α-triazine.	Black to yellow on warming. (The former probably partially decomposes to piperidene.)
2-Thio-4-carbethoxy-5:5-dimethyl-thiazolidine.	No change.
Dimethylglyoxime.	Black to brownish-yellow on warming.
Diphenylcarbazide.	Black to yellow-brown in the cold; becoming deep crimson on standing.

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10. The following classes of compounds do not react with the reagent:	Hydrocarbons, halogenohydrocarbons, aldehydes, ketones, ethers, amino-acids, nitro-compounds, nitriles, esters and simple sugars.

Conclusion. Vanadium 8-hydroxyquinolate is a specific reagent for the detection of alcohols, a colour change from black to red in the cold being a positive reaction. Only those alcohols which are completely insoluble in tetrachloroethane (*e.g.* mannitol and simple sugars) do not react. The reagent is not completely specific for amines; the majority give a golden yellow colour, but some react very slowly and others not at all. All thiols react in a fairly uniform manner, but some amines react to give a golden yellow colour which is not easily distinguishable from the lemon yellow produced by thiols. The *o*-dichlorobenzene solution may be used as a reagent for acidic substances: a colour change from black to blue is caused by low molecular-weight carboxylic acids, phenols and all hydrochlorides[4]. (If any substance which is not dry is added to the reagent in *tetrachloroethane* and the solution warmed, the black colour changes to blue.)

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Notes: (i) The mixture should not be heated strongly when testing for alcohols, as the red colour of the solution fades at high temperatures. However, in nearly all instances, except in those of some cyclic alcohols, the colour returns on cooling.

(ii) Most compounds that do not react with the reagent, do not interfere with the alcohol reaction, but phenols (including 8-hydroxyquinoline) and low molecular-weight carboxylic acids inhibit the colour change from black to red when only small amounts of the alcohol are present.

(iii) The tetrachloroethane used in making up the reagent solution must be dry, if the damp solvent is used, the solution may become blue on long standing. The blue solution gives the same reactions as the black solution, but is less sensitive to small amounts of alcohols, since the colour change is inhibited by acids.

(iv) Similar results are obtained by using a tetrachloroethane solution of the green anhydride of vanadium 8-hydroxyquinolate, $(C_9H_6ON)_2 = VO\text{-}O\text{-}VO = (C_9H_6ON)_2$, which is prepared by heating the black complex at 250° C for 30 minutes or by the prolonged boiling of its solution in tetrachloroethane under a dry atmosphere. However, the green solution is not recommended as a reagent as it is not possible to detect small quantities of thiols or amines with it.

(v) *o*-Dichlorobenzene is an excellent solvent for vanadium 8-hydroxyquinolate and may be used in place of tetrachloroethane for preparing the reagent solution. The complex dissolves readily on warming to give a black solution and the colour does not change to blue on heating, even if the solvent is moist, because *o*-dichlorobenzene is not readily hydrolyzed. On heating the solution to boiling (180° C), the colour fades to a light yellow and returns to black on cooling. This black solution gives the same reactions as the tetrachloroethane solution in nearly all instances, except that it is not turned blue by acids so readily.

Detection of ethyl alcohol in aqueous media

If the reagent is shaken with aqueous alcohol, the usual colour change from black to red occurs, the time required for a visible change depending on the alcohol concentration. The following reactions were obtained on typical aqueous solutions:

Wine. On shaking the reagent with an equal volume of wine, the black colour changed to red almost immediately. (No red colour is extracted from wine by pure tetrachloroethane.)

Beer. The emulsion formed on shaking the reagent with beer takes a long time to separate into two distinct layers; the black colour of the reagent layer had changed to a dark purple in two hours and to red on standing overnight. No colour is extracted from beer by pure tetrachloroethane.

Blood. If blood was shaken with the reagent a red emulsion resulted and no colour change could be observed. The blood was centrifuged to remove the red corpuscles, and the clear liquid shaken with an equal volume of reagent solution of half the usual concentration. Blood containing 1% of alcohol gave a tositive test in three hours, whereas normal blood gave no reaction on standing in contact with the reagent overnight.

Sensitivity of the alcohol-detection reaction

It was found that a ratio of 50 molecules of a primary alcohol, 100 molecules of a secondary alcohol or 500 molecules of a tertiary alcohol to one molecule of vanadium 8-hydroxy-quinolate gave a positive reaction in 10-15 minutes.

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The minimum satisfactory concentration for the reagent solution is $10^{-4}M$. In a micro-centrifuge-cone, the colour change may be seen with 0.1 ml of reagent + 0.1 ml of test solution. With a molecular ratio of 50 : 1, this corresponds to approximately 20 μg of ethanol in 0.1 ml. Dilution limit: 1 in 5000.

Similarly for the butanols, the limits are:

40 μg *n*-butanol at a dilution limit of 1 in 2500,
80 μg of *sec*-butanol at a dilution limit of 1 in 1250, and
400 μg of *tert*-butanol at a dilution limit of 1 in 250.

If the alcohol is left in contact with the reagent for 24 hours, a positive reaction is obtained with a molecular ratio of 12 : 1, 25 : 1 and 125 : 1 for primary, secondary and tertiary alcohols respectively.

Light-absorption curves

Light-absorption curves, measured in 1 cm cells with a Uvispek Spectrophotometer, are given for solutions of vanadium 8-hydroxyquinolate in tetrachloroethane (Fig. 1):

(a) Black solution in anhydrous solvent.
(b) Blue solution obtained by heating in moist solvent.
(c) Red solution obtained by addition of an excess of ethanol.
(d) Yellow solution obtained by addition of an excess of ethyl mercaptan.
(e) Yellow solution obtained by addition of an excess of *n*-butylamine.

all of which contained 7.3 mg of vanadium 8-hydroxyquinolate in 100 ml.

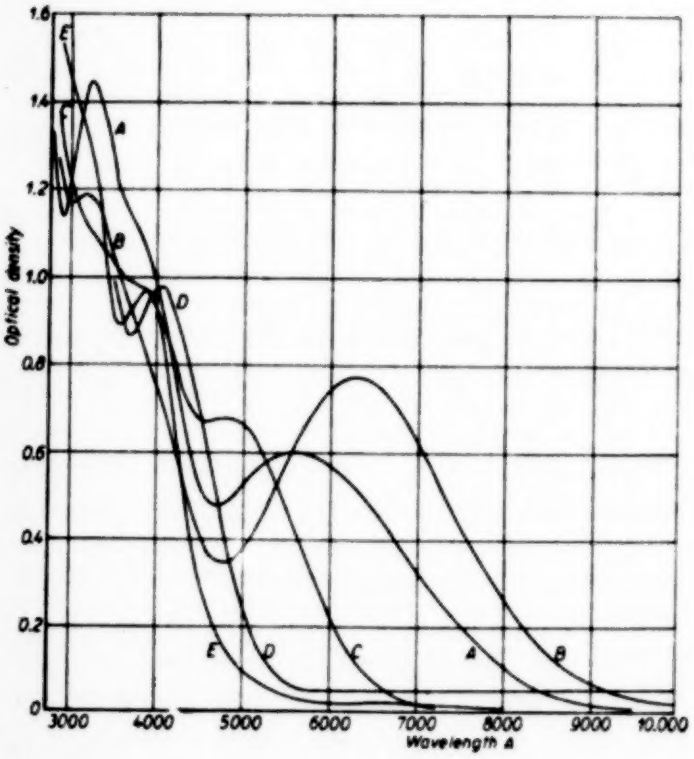

Fig. 1. Absorption curves of vanadium 8-hydroxyquinolate in tetrachloroethane.
A. Black solution in anhydrous solvent.
B. Blue solution obtained by heating in moist solvent.
C. Red solution obtained by addition of an excess of ethanol.
D. Yellow solution obtained by addition of an excess of ethyl mercaptan.
E. Yellow solution obtained by addition of an excess of butylamine.
All these solutions contained 7.3 mg of vanadium 8-hydroxyquinolate per 100 ml.

Conversion of vanadium 8-hydroxyquinolate to the red form with increasing quantities of various alcohols

It is seen from the absorption-curves that the red form has virtually no absorption above 7000 A, while the black form absorbs up to 10000 A. If the optical density is measured at 7000 A, the progress of the reaction may be followed.

Batches of solutions, all containing the same concentration of vanadium 8-hydroxyquinolate, and containing increasing molecular ratios of ethyl, cetyl, *n*-butyl, *sec*-butyl and *tert*-butyl alcohols were prepared. The optical density of each member of each batch was measured at 7000 A in a 1 cm cell with a Unicam S.P. 600 Spectrophotometer; and curves were plotted of optical density against the molecular ratio of the alcohol to the complex. Fig. 2 shows the curves obtained when the solutions had reached equilibrium, (after about a week). Smooth curves were obtained in all instances, whether equilibrium had been reached or not, provided that measurements on all members of a batch were made at the same times after mixing the reagents.

By comparison with a set of standards, the reagent may be used for the semi-quantitative determination of alcohols, in the absence of interfering substances. For quantitative use, the greatest accuracy is obtained if quantities are chosen to give a molecular ratio of between 10 and 50 of the alcohol to one of vanadium 8-hydroxyquinolate (for *p*- and *sec*-alcohols). It must be stressed that the standards must be treated under conditions identical to those of the test solutions, as the intensity, which appears to be dependent on an equilibrium between the black and the red forms, is sensitive to temperature.

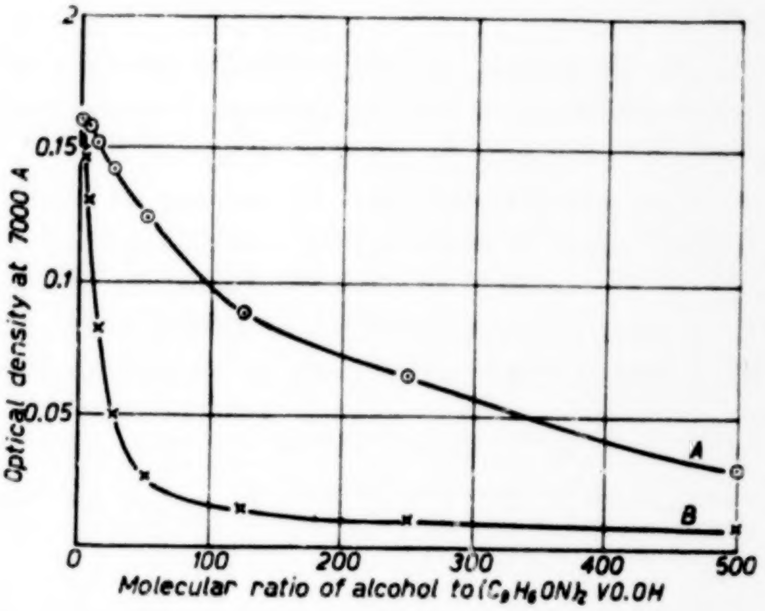

Fig. 2. Curves showing the relation between optical-density at 7000 A and molecular ratio of alcohol to vanadium 8-hydroxyquinolate in tetrachloroethane; the solutions having reached equilibrium. A. *tert*-butyl alcohol, B. *n*-butyl alcohol. Curves almost identical with B. were given by ethyl, *sec*-butyl and cetyl alcohols.

Relative effect of active groups on the reagent, and interconversion of the reaction products

1. *Alcohols and mercaptans*

(a) Addition of a large excess of ethyl mercaptan to a solution turned red by approximately 100 molecular equivalents of ethyl alcohol caused a slow change from red through orange to yellow.

(b) Upon addition of a large excess of ethyl alcohol to a solution turned greenish-yellow by a small quantity of ethyl mercaptan, the colour slowly deepened through orange to red.

2. *Alcohols and amines*

(a) Addition of a drop of *iso*-propylamine to a red solution containing a large excess of ethyl alcohol caused a fairly rapid fading of the colour through orange to yellow.

(b) Addition of a very large excess of ethyl alcohol to a yellow solution containing a trace of *iso*-propylamine produced no immediate effect, the solution became orange-red on standing overnight.

3. *Alcohols and acids*

The blue form of vanadium 8-hydroxyquinolate is less sensitive to small quantities of alcohols than the black form. Addition of acids (the lower carboxylic acids or phenols) to a red solution caused a partial reconversion to the blue form when only small quantities of alcohol were present.

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4. *Mercaptans and acids*

On addition of ethyl mercaptan to a solution of vanadium 8-hydroxyquinolate in tetrachloroethane turned blue by acetic acid, the colour changed to green or yellow depending on the quantity of mercaptan. Addition of much acetic acid to the green or yellow solution produced no colour change, but formic acid caused the colour to revert to blue.

5. *Acceleration of the reaction with alcohols by bases*

That the colour change from black to red with alcohols is accelerated by bases is shown by the fact that ethanolamine reacts much more quickly than ethanol and by the following experiment: 2 drops of ethanol were added to 1 ml of the reagent, followed by a drop of *n*-butylamine. The colour immediately changed from black to orange-red and slowly faded to yellow; a blank, containing the same quantities of alcohol and the reagent took a few minutes to become red.

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SUMMARY

The 8-hydroxyquinolate of pentavalent vanadium ("vanadium 8-hydroxyquinolate", $(C_9H_6ON)_2 \cdot VO.OH$) dissolves in a number of chlorohydrocarbons to give deep blue-black solutions. These solutions undergo distinctive colour changes upon addition of acids (blue), alcohols (red *via* purple), thiols (yellow *via* green) and amines (yellow *via* green), provided that these reagents are soluble in the chlorohydrocarbon. These sensitive and specific qualitative tests are extended to the semi-quantitative determination of alcohols. For comparable compounds the rate of reaction with vanadium 8-hydroxyquinolate is as follows: $[-NH_2, =NH, \equiv N] > [-CH_2OH, -CH_2SH] > [=CHOH, =CHSH] > [\equiv COH, \equiv CSH]$.

RÉSUMÉ

Le 8-hydroxyquinoléate de vanadium (V), $(C_9H_6ON)_2$ VO.OH, est soluble dans un certain nombre d'hydrocarbures chlorés en donnant des solutions bleu noir. Ces solutions changent de couleur par addition d'acides (bleu), d'alcool (rouge, en passant par pourpre), de thiols (jaune, en passant par vert), d'amines (jaune, en passant par vert), à condition que ces réactifs soient solubles dans l'hydrocarbure chloré. Ces réactions qualitatives, sensibles et spécifiques, peuvent être utilisées pour le dosage semiquantitatif des alcools. La nature des substituants influence la vitesse de réaction avec l'hydroxyquinoléate de vanadium. Pour des composés analogues, cette vitesse de réaction varie dans l'ordre suivant: $[-NH_2, =NH, \equiv N] > [-CH_2OH, -CH_2SH] > [=CHOH, =CHSH] > [\equiv COH, \equiv CSH]$.

ZUSAMMENFASSUNG

Das 8-Hydroxychinoleat von Vanadium (V) $(C_9H_6ON)_2VO.OH$, ist in einer gewissén Anzahl von Chlorkohlenwasserstoffen löslich und gibt schwarz blaue Lösungen. Diese Lösungen ändern ihre Farbe durch Zugabe von Säure (blau), von Alkohol (geht es über purpur zu rot), von Thiol (über grün zu gelb) von Aminen (über grün zu gelb) unter der Bedingung dass diese Reaktive in Chlorkohlenwasserstoff löslich sind. Diese qualitativen Reaktionen, empfindlich und speziefisch, können für semiquantitative Alkoholbestimmungen verwendet werden. Die Art der Substituenten beeinflusst die Reaktions-Geschwindigkeit mit Vanadium-hydroxychinolein. Für analoge Verbindungen variiert diese Reaktions-Geschwindigkeit in folgender Ordnung: $[-NH_2, =NH, \equiv N] > [-CH_2OH, -CH_2SH] > [=CHOH, =CHSH] > [\equiv COH, \equiv CSH]$.

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VOLUMETRIC ESTIMATION OF POTASSIUM PERMANGANATE AND POTASSIUM DICHROMATE IN MIXTURES WITH OXALIC ACID

by

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A simple and direct method for the estimation of permanganate and dichromate existing in mixtures does not appear to have been proposed so far. A method recommended by VOGEL[1] for adoption in connection with steel analysis consists in eliminating the permanganate by treating the mixture at boiling temperature with a solution of either (i) dilute hydrochloric acid (1:3) or (ii) sodium azide. When all the permanganate is destroyed, the dichromate left over is estimated by adding a known excess of ferrous ammonium sulphate and titrating the unreacted ferrous ammonium sulphate with a standard solution of dichromate. This method is subject to two disadvantages. When the mixture of potassium permanganate and dichromate is heated with hydrochloric acid in order to eliminate the permanganate, it is possible that part of the dichromate is also lost. Moreover, the amount of permanganate present in the mixture is not estimated directly by this method, but is only computed by difference.

We investigated the possibility of making use of the familiar reaction between oxalic acid and permanganate for the differential titration of permanganate in presence of dichromate. It is well known from the work of DHAR[2] and others on the kinetics of the reaction between chromic acid and oxalic acid, that the reaction is quite slow at the room temperature even when catalysed by manganous salts. But manganous sulphate catalyses the reaction between oxalic acid and permanganate to such a degree that it is possible to achieve the titration of oxalic acid by permanganate even at the room temperature. Hence, a large series of experiments was conducted in various ways to ascertain the conditions under which an accurate differential estimation of permanganate could be made with oxalic acid in the presence of dichromate.

EXPERIMENTAL

TITRATION OF OXALIC ACID WITH PERMANGANATE AT ROOM TEMPERATURE

In the following experiments an aliquot volume of standard sodium oxalate taken in an Erlenmeyer flask is mixed with sufficient sulphuric acid and manganous sulphate and titrated with potassium permanganate from the burette at room temperature (18° C). The amount of manganous sulphate is varied to ascertain the optimum concentration required to enable a rapid and accurate titration to be carried out. The results are recorded in Table I.

TABLE I

VARIATION OF THE CONCENTRATION OF THE CATALYST

10 ml of oxalic acid + 10 ml H_2SO_4 (1:1) + X ml $MnSO_4$ ($M/40$) + water to make up to about 100 ml

Vol. of $MnSO_4$ solution added in ml (X)	*Permanganate consumed in ml*
0.2	Reaction is very slow
0.5	10.20
1.0	10.20
2.0	10.20
3.0	10.20
4.0	10.20
5.0	10.20
*6.0	10.40

In the last experiment (*) and in others containing higher amounts of $MnSO_4$, manganese dioxide is precipitated and this interferes in the detection of the end-point. Hence, results higher than the theoretical are obtained. It may also be noted that, if the amount of manganous sulphate is not sufficient, the reaction is not rapid for the titration to be carried out. The concentration of sulphuric acid should also be sufficient, otherwise, manganese dioxide is again precipitated with the consequent risk of overstepping the end-point. From a large number of experiments, it has been concluded that an overall concentration of about $2N$ sulphuric acid and an overall concentration of $5.0 \cdot 10^{-5}$ molar manganous sulphate are quite adequate for the rapid titration of oxalic acid to be carried out at the room temperature. About 90 seconds was taken for each titration.

In the next series of experiments, an aliquot volume of standard sodium oxalate solution is taken in an Erlenmeyer flask along with sulphuric acid and manganous sulphate at the concentration mentioned above and titrated with a mixture of permanganate and dichromate of known composition run from a burette. The titration is stopped as soon as a permanent orange-red colour is imparted to the solution. It was noticed during the titration that as the mixture is added, the permanganate interacts rapidly with the oxalic acid but not so the dichromate so that the dichromate accumulates in the solution imparting an yellow colour. When all the oxalic acid has reacted, a drop in excess of the mixture in the burette introduces excess permanganate. This, along with the accumulated dichromate already present in the mixture, imparts a characteristic orange-red colour to the solution. The volume run in is therefore corrected for one drop. The results are recorded in Table II.

TABLE II

5 ml of oxalic acid (0.1042N) + 10 ml H_2SO_4 (1:1) + 2.0 ml $MnSO_4$ + Water to make up to 90 ml.
5 ml of oxalic acid = 5 ml permanganate

Composition of permanganate — dichromate mixture $KMnO_4$(A) — 0.1042N $K_2Cr_2O_7$(B) — 0.1042N (1)	(2)	*Vol. of mixture run in* (3)	*Vol. of 0.1042N $KMnO_4$ present in the mixture run in and reacting with oxalic acid (X)* (4)	*Volume of 0.1042N $K_2Cr_2O_7$ solution in the mixture run in reacting with oxalic acid (Y)* (5)	*Induction Factor = Y/X = mols of oxalic acid reacting with $K_2Cr_2O_7$ / mols of oxalic acid reacting with $KMnO_4$* (6)
1	20 ml A + 30 ml B	8.95 ml	3.58 ml	5.0 — 3.58 = 1.42 ml	0.397
2	40 ml A + 10 ml B	4.85 ml	3.88 ml	5.0 — 3.88 = 1.12 ml	0.289
3	70 ml A + 10 ml B	4.75 ml	4.17 ml	5.0 — 4.17 = 0.83 ml	0.199
4	90 ml A + 10 ml B	4.95 ml	4.46 ml	5.0 — 4.46 = 0.54 ml	0.121
5	190 ml A + 10 ml B	4.85 ml	4.60 ml	5.0 — 4.60 = 0.40 ml	0.087

Knowing the composition of the mixture, one can calculate the amount of permanganate present in the mixture run in. These results are given in column (4) of Table II. We know that the oxalic acid taken is equivalent to 5 ml of the given permanganate solution. If we deduct from this the corresponding values of permanganate reacted we get the amount of dichromate (from the mixture run in) that has reacted with oxalic acid. These values are given in column (5). If none of the dichromate from the mixture has reacted with the oxalic acid, the figures in column (5) should have been zero and all the figures in column (4) should have been 5 ml. But the results are otherwise; they show that when a mixture of permanganate and dichromate is run from a burette into an acidified solution of oxalic acid, containing manganous sulphate, both the permanganate and dichromate react with the oxalic acid. All the observations show that all the permanganate present in the mixture run in reacts with the oxalic acid, while only a part of the dichromate present therein reacts with oxalic acid. From this, it is evident, that the reaction between dichromate and oxalic acid induces the reaction between dichromate and oxalic acid. The ratio of the number of moles of oxalic acid reacting with dichromate to the number of moles of oxalic acid reacting with permanganate may be defined as the induction factor. From the results presented in the Table II it is seen that the induced reaction is manifest even though the ratio of permanganate to dichromate is widely varied. When the inductor ($KMnO_4$) concentration is increased relatively to the concentration of the acceptor ($K_2Cr_2O_7$), the value of the induction factor diminishes. In view of the interference of the induced reaction, this mode of titration is not useful for the estimation of permanganate in mixtures with dichromate. Hence, the mode of titration is altered as follows. An aliquot volume of the given mixture of permanganate and dichromate is taken in an Erlenmeyer flask and treated with appropriate quantities of sulphuric acid and manganous sulphate and then titrated with a standard solution of oxalic acid taken in a burette. It has been observed, that under these conditions the oxalic acid reacts only with permanganate present in the mixture and not with the dichromate. The unreacted dichromate in the mixture is then estimated with a standard solution of ferrous ammonium sulphate using an internal indicator after adding the necessary quantity of syrupy phosphoric acid.

Numerous experiments have shown that the oxalic acid consumed in the first stage of the titration gives a measure of the permanganate and the ferrous ammonium sulphate consumed in the second stage of the titration gives a measure of dichromate. Hence, we propose the following procedure for the estimation of the individual constituents in a mixture of permanganate and dichromate.

Procedure

A known volume of the mixture of potassium permanganate and dichromate is taken in an Erlenmeyer flask, 10 ml of (1:1) sulphuric acid are then added, followed by 2 ml of $M/40$ manganous sulphate solution. The solution is then diluted to about 100 ml. It is titrated with oxalic acid solution of known concentration until the brownish-red colour of the mixture changes to a deep yellow colour. The colour change at the end-point is quite sharp. The volume of oxalic acid reacted is noted and from this value, the amount of potassium permanganate present in the mixture is calculated. To the dichromate left over in the Erlenmeyer flask, 5 ml of syrupy phosphoric acid (sp. gr. 1.7) are added. The solution is then titrated with a standard ferrous ammonium sulphate solution, adding an internal indicator towards the end. 0.5 ml of a 0.1% solution of diphenylbenzidine in concentrated sulphuric acid is used for this purpose. The titration is carried on till the blue colour of the indicator is discharged. The amount of dichromate can be calculated, knowing the normality and the volume of ferrous ammonium sulphate run in.

Numerous assays have been made with mixtures of permanganate and dichromate of varying composition, prepared by mixing different volumes of $0.1121N$ potassium permanganate and $0.1285N$ potassium dichromate. For all the estimations $0.1042N$ oxalic acid and $0.1221N$ ferrous ammonium sulphate solution have been used. The results obtained are recorded in Table III.

From Table III it will be clear that both permanganate and dichromate can be estimated accurately in mixtures by the method now proposed. Chemical induction does not interfere in these titrations. The accuracy of the method is not affected by wide variations in the relative proportions of permanganate and dichromate.

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TABLE III

Composition of the mixture $KMnO_4:K_2Cr_2O_7$	*Amount of permanganate*		*Amount of dichromate*	
	taken	*found*	*taken*	*found*
1:1	0.01765 g	0.01765 g	0.0315 g	0.0315 g
2:1	0.02362 ,,	0.2365 ,,	0.0209 ,,	0.0209 ,,
1:2	0.01180 ,,	0.01180 ,,	0.0420 ,,	0.0420 ,,
4:3	0.02030 ,,	0.02030 ,,	0.0270 ,,	0.0269 ,,
3:4	0.01520 ,,	0.01520 ,,	0.0360 ,,	0.0360 ,,
9:1	0.03200 ,,	0.03190 ,,	0.0063 ,,	0.0063 ,,
1:9	0.00350 ,,	0.00350 ,,	0.0567 ,,	0.0567 ,,
1:15	0.00440 ,,	0.00440 ,,	0.0118 ,,	0.0118 ,,
10:1	0.03367 ,,	0.03366 ,,	0.0032 ,,	0.0032 ,,

SUMMARY

1. A simple method has now been developed for the volumetric estimation of potassium permanganate and potassium dichromate in mixtures. The method consists in taking an aliquot volume of the mixture in an Erlenmeyer flask, adding sufficient quantities of sulphuric acid and manganous sulphate (catalyst) and titrating with a standard solution of sodium oxalate or oxalic acid run in from the burette, until the colour changes from orange-red to yellow. The oxalic acid run ingives a measure of the permanganate present in the mixture. Then the mixture in the flask is titrated with a standard solution of Mohr's salt using diphenylbenzidine as indicator. The volume of Fe^{+2} solution run in the second stage gives a measure of the dichromate present in the original mixture.

2. The reverse titration does not give accurate results because it is affected by the induced reaction between oxalic acid and dichromate which is induced by the reaction between oxalic acid and permanganate during the first stage of the reaction. This induced reaction has been studied in some detail.

RÉSUMÉ

1. Une méthode simple est proposée pour le dosage volumétrique de mélanges de permanganate et de dichromate de potassium. Elle consiste à prélever une partie aliquote du mélange à analyser, à lui ajouter une quantité suffisante d'acide sulfurique et de sulfate de manganèse (catalyseur) et à titrer au moyen d'une solution étalon d'oxalate de sodium ou d'acide oxalique jusqu'à virage au jaune. L'acide oxalique utilisé permet de calculer la teneur en permanganate. Le mélange est ensuite titré par une solution étalon de sel de Mohr en présence de diphénylbenzidine comme indicateur. Le volume de la solution de Fe^{+2} utilisé donne la teneur en dichromate du mélange.

2. La titration inverse ne donne pas des résultats précis, il se produit une réaction entre l'acide oxalique et le dichromate, induite par la réaction: acide oxalique-permanganate, pendant le premier stade de la réaction. Cette réaction d'induction a été étudiée.

ZUSAMMENFASSUNG

1. Es wird eine einfache Methode vorgeschlagen, um Mischungen von Kaliumpermanganat und Kaliumbichromat volumetrisch zu bestimmen. Sie besteht darin einen aliquoten Teil der zu bestimmenden Mischung zu entnehmen, eine genügende Menge Schwefelsäure und Mangansulfat (Katalysator) beizufügen und das Ganze mit einer Vergleichslösung von Natriumoxalat oder Oxalsäure bis zum gelben Umschlagspunkt zu titrieren. Die verbrauchte Oxalsäure erlaubt den Gehalt an Permanganat zu errechnen. Darauf wird die Mischung mit einer Vergleichslösung von Mohrschem Salz titriert in Anwesenheit von Diphenylbenzidin als Indikator. Das Volumen der verbrauchten Fe^{+2}-Lösung gibt den Gehalt an Bichromat in der Mischung.

2. Die inverse Titration gibt keine genaue Resultate, da eine Reaktion zwischen der Oxalsäure und dem Bichromat stattfindet. Diese wird induziert durch die Reaktion: Oxalsäure-Permanganat, während des ersten Stadiums der Reaktion. Diese Induktionsreaktion wurde untersucht.

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THE DETERMINATION OF MICROGRAM QUANTITIES OF ORGANIC NITROGEN

by

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INTRODUCTION

The Kjeldahl method for the determination of nitrogen is probably one of the most well established in the fields of both macro and micro organic analysis. There is, however, a minimum limit to which the method can be applicable, and the development of this sub-micro method was undertaken to extend the lower limits of determination without loss of general applicability and simplicity. Research studies in which small changes in nitrogen content are of paramount importance have been successfully carried out using the method described in this report. There are numerous publications dealing with modifications of the Carlsberg methods[1] and sub-micro Kjeldahl determinations[2], also adaptations using sealed tube digestion[3] and diffusion methods[4]. All of these methods, however, involve the use of special equipment, are time consuming, and are of specific rather than general application.

The reaction of sodium hypobromite reagent with ammonia, $3NaBrO + 2NH_3 = N_2 + 3NaBr + 3H_2O$ is well-known in the clinical determination of urea, when the volume of nitrogen evolved is measured. Recently, the reaction was used by HARVEY[5] to estimate 5-30 microgram quantities of nitrogen, *in situ*, in unicellular algae by measuring the reagent consumed. HARVEY's method is also of only limited application, since the sample size is very restricted, and the method is unsuitable for materials of unknown origin, or samples known to contain inorganic radicals or elements, since these will often interfere with the hypobromite reaction to give ambiguous results.

The method now described has few limitations, since sample size can vary from 0.2-200 mg according to nitrogen present. Tables I-III illustrate these limits. Table III indicates the extent to which the accuracy of the method falls off as the nitrogen content decreases. In order to obtain greater accuracy at this level the increased sample required (about 1 g) would necessitate large increases in reagent. This, in turn, would result in further possible inaccuracies. Table IV gives some idea of the quantity of reagent consumed by nitrogen from reagents, which would often exceed the amount of sample nitrogen. The type o nitrogen compounds which require reduction with hydriodic acid and red phosphorus, such as nitro, nitroso, azoxy and phenyl hydrazines can be determined, the pretreatment being carried out before Kjeldahl digestion.

The sensitivity of this method is such that all reagents should be accurately measured

and the entire operation must be carried out away from chemical contaminants of any kind, in order to obtain fully reproducible results. A special stand to accommodate all reagents and give automatic delivery is in course of preparation.

Mechanism of reactions involved and calculation

$$1.\ 3NaBrO + 2NH_3 = 3NaBr + 3H_2O + N_2$$

$$2.\ 2Na_2S_2O_3 + O(NaOBr) + H_2O = Na_2S_4O_6 + 2NaOH$$

$$\therefore \%\ \text{nitrogen} = \frac{(a\text{-}b) \times F \times 466.6}{\text{sample weight (mg)}}$$

where a = blank titration
b = sample titration
F = normality of sodium thiosulphate

METHOD

Reagents

1. Sulphuric acid.
2. Catalyst — grind together to a *fine powder*
   (a) 150 g potassium sulphate
   (b) 10 g mercuric oxide
   (c) 5 g selenium
3. Sodium hydroxide — 48% w/v.
4. Sodium thiosulphate — 44% w/v.
5. Hydrochloric acid — 1% v/v.
6. Alkaline hypobromite — a stock solution is prepared by dissolving 1g of sodium hydroxide, 23 g of sodium carbonate and 0.5 ml of bromine in 1 litre of water (see note). Store in a glass-stoppered amber bottle. Reagent strength solution: — dilute the stock solution with an equal volume of water.
7. Buffer solution — 40 g potassium hydroxide, 6 g boric acid in 100 ml water.
8. Potassium iodide — 20% w/v.
9. Acetic acid — dilute 2 parts of glacial acetic acid with 1 part of water.
10. Standard sodium thiosulphate — dilute standard $N/10$ solution to $N/500$ as required. The dilute solution should not be used for more than one day.
11. Sodium starch glycollate — dissolve 0.2 g in 10 ml water and shake.
12. Thymolphthalein solution.

Note. The ultimate strength of this solution varies somewhat from batch to batch, since slight variations in the amount of bromine added cannot easily be avoided.

Procedure

Weigh out in glass capsules samples containing approximately 0.1 mg nitrogen, provided the weight of sample does not exceed 200 mg. Add sulphuric acid and catalyst weighed accurately on an analytical balance, as follows:

Wt sample mg	*Catalyst g*	*Acid ml*	*Additional digestion time*
0.2-5	0.5	2	15 min
5-50	1.0	3	20 ,,
50-200	1.5	4	30 ,,

Digest until the mixture becomes clear yellow, and for a further period as above. With each series of determinations carry out blank analyses to correspond with the digestion conditions.

Transfer the mixture to the reaction flask of a micro-Kjeldahl distillation unit, using the same amount of water to complete the transfer in each determination. Place a 150 ml conical flask (painted white over the area to contain solution and titrant) containing 10 ml of 1% hydrochloric acid under the condenser, whose tip should dip into the solution. Add to the reaction flask 6 ml (9 ml, 12 ml) sodium hydroxide solution, mix the contents by admitting steam, then add 2 ml (3 ml, 4 ml) sodium thiosulphate solution. Wash down the delivery tube so that the solution level in the flask reaches a predetermined mark, and steam distil until the receiver contains 25 ml solution. It is advisable to mark the flasks at the 25 ml level.

Determine the amount of buffer solution required to bring the pH of the acid absorbent to 8.5-9.6, by titrating 10 ml with the buffer solution until thymolphthalein attains a pale blue colour.

Add to the distillate 5 ml of sodium hypobromite, followed by the predetermined amount of buffer solution. After a few seconds add 1 ml of potassium iodide solution and 2 ml of acetic acid. Titrate the liberated iodine to a pale yellow colour with *N*/500 sodium thiosulphate, add a few drops of sodium starch glycollate, and titrate to the complete disappearance of the blue colour. The end-point is more readily determined in a flask protected from direct daylight in the manner already described.

RESULTS

TABLE I

RESULTS OBTAINED FOR PURE ORGANIC COMPOUNDS

Compound	*Sample* *mg*	*Blank* *ml N/500 thio*	*Titration* *ml N/500 thio*	*Nitrogen* *Found*	*Nitrogen* *Theory*
Benzanilide	0.500	16.1	12.3	7.09	7.10
	0.382	16.1	13.2	7.08	
Caproamide	+0.81	16.4	6.1	11.9	12.16
	0.81	16.4	5.8	12.2	
Benzidine	+0.306	16.5	11.5	15.25	15.2
	0.306	16.5	11.5	15.25	

+ Aliquots of solution taken

TABLE II

COMPOUNDS PRETREATED WITH HYDRIODIC ACID

Compound	*Sample* *mg*	*Blank* *ml N/500 thio*	*Titration* *ml N/500 thio*	*Nitrogen* *Found*	*Nitrogen* *Theory*
Picric acid	0.229	21.9	17.4	18.3	18.35
	0.399	21.9	14.0	18.5	
2.4 di NO_2 Ø hydrazine	0.286	20.1	11.8	27.1	28.25
	0.182	20.1	14.45	28.9	
α nitroso-β naphthol	0.384	15.6	12.3	8.0	8.1
	0.472	15.6	11.3	8.5	

TABLE III

THE DETERMINATION OF NITROGEN IN AQUEOUS SOLUTIONS OF LAURYLETHANOLAMIDE

Sample fraction	*Weight* *g*	*Blank* *ml N/500 thio*	*Titration* *ml N/500 thio*	*% Nitrogen*
1	0.2208	12.8	6.95	0.024
	0.2252		7.1	0.025
2	0.2505		3.9	0.033
	0.2199		4.7	0.034
3	0.2057		7.5	0.024
	0.2573		6.5	0.023
4	0.2103		10.5	0.010
	0.2289		9.0	0.015
5	0.2143		12.0	0.003
	0.2485		11.15	0.006
6	0.1989		11.95	0.004
	0.2311		12.6	0.001

TABLE IV

Catalyst g	*Acid* ml	*Sodium hydroxide* ml	*Sodium thiosulphate* ml	*Titration of 5 ml reagent* directly	as analysis blank
0.5	2	6	2	13.7	12.8
1.0	3	9	3	20.6	19.2
1.5	4	12	4	20.6	18.6
10	25	80	30	26.5	20.5
10	35	120	30	26.5	10.5

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SUMMARY

A method is described for the determination of microgram quantities of nitrogen in a wide variety of materials. This method involves the Kjeldahl procedure for the conversion of nitrogen to ammonium or amine sulphate. Digestion of the sample with concentrated sulphuric acid and catalyst, and, if necessary, pretreatment with hydriodic acid and red phosphorus, are followed by steam-distillation into a dilute acid solution. The final determination depends on the reaction of ammonia, in a suitably buffered solution, with sodium hypobromite reagent, and measurement of the excess reagent by titration of the iodine liberated by it from acidified potassium iodide, with a standard $N/500$ sodium thiosulphate solution, using sodium starch glycollate indicator.

Since sample size is relatively unrestricted and the final titration can measure 5 micrograms of nitrogen, the sensitivity of the method is very high.

Reference is made to existing sub-micro methods which, although sensitive, are time-consuming and specific in application.

RÉSUMÉ

Une méthode de Kjeldahl est décrite pour le dosage de micro-quantités d'azote dans des substances très variées. La digestion de l'échantillon à analyser dans l'acide sulfurique concentré, en présence d'un catalyseur et éventuellement le traitement préalable avec l'acide iodhydrique et le phosphore rouge sont suivis d'une distillation dans une solution d'acide dilué. Le dosage final est basé sur la réaction de l'ammoniac avec l'hypobromite de sodium en solution tampon appropriée; on mesure l'excès de réactif par titration de l'iode libéré, après addition d'iodure de potassium en solution acide, au moyen d'une solution étalon de thiosulfate de sodium $N/500$, en présence d'amidon-glycollate de sodium comme indicateur. La grandeur de la prise n'étant relativement pas limitée et la titration finale permettant de doser jusqu'à 5 μg d'azote, la sensibilité de cette méthode est très grande.

ZUSAMMENFASSUNG

Eine Methode nach Kjeldahl ist beschrieben um Mikroquantitäten von Stickstoff in sehr verschiedenen Substanzen zu bestimmen. Der Aufschluss der zu analysierenden Substanz mit konzentrierter Schwefelsäure, in Gegenwart eines Katalysators und eventuel eine vorherige Behandlung mit Iodsäure und rotem Phosphor gehen einer Destillation in einer verdünnten Säurelösung voran. Die Endbestimmung basiert auf der Reaktion von Ammoniak mit Natriumhypobromit in einer geeigneten Pufferlösung. Man misst den Überschuss des Reaktivs durch Titration des freien Iodes, nach Zugabe von Kaliumiodid in saurer Lösung, mit Hilfe einer Vergleichslösung von Natriumthiosulfat $N/500$, in Gegenwart von Stärke-Natriumglykollat als Indikator. Da die Grösse der Einwaage relativ nicht begrenzt ist, und die Endtitration eine Bestimmung bis zu 5 μg Stickstoff erlaubt, ist die Empfindlichkeit dieser Methode sehr gross.

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THE MICRO AND SEMIMICRO DETERMINATION OF ALKOXYL GROUPS

by

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A method for the determination of alkoxyl groups on the semimicro scale, based on the method of VIEBÖCK AND BRECHER[1], has been in use in this Department for many years. When its application was extended to an increasing variety of research compounds it was found in certain cases that erratic results were obtained. An extensive re-examination of the method has, therefore, been carried out.

Although no fundamental change has been made in the procedure for decomposing the sample since ZEISEL[2] first advanced the method, some difficulties often occur in dissolving certain types of organic compound before the decomposition with hydriodic acid. Errors may arise owing to the boiling hydriodic acid being carried over by bumping, whilst the purity of the hydriodic acid itself has been regarded by many workers as a critical factor in the method. The wash liquids used for scrubbing alkyl iodides have been the subject of extensive investigations [3,4,5], but there does not appear to be unanimity as to the most suitable, particularly when the sample contains sulphur. An explanation of the use of two alkali acetates (potassium acetate in the absorbent and a sodium acetate buffer in the titration) is still awaited. Finally, the design of the apparatus leaves room for improvement, particularly with regard to the elimination of bromine fumes.

The above factors have each been investigated and the findings are summarized below. As a result of this study a semimicro apparatus, which with suitable modification may be used on the micro scale, has been developed. The method we finally propose is applicable to the determination of methoxyl or ethoxyl groups.

α-Methyl-D-glucoside and phenacetin have been used as the main reference substances in the investigation.

Solution of sample

It was found preferable to dissolve the sample in a suitable solvent before the addition of hydriodic acid, but the quantity of this solvent had to be kept to a minimum so as to avoid any possibility of diminishing the effective strength of the hydriodic acid. The use of phenol alone, as recommended in the A.O.A.C. semimicro procedure[6] does not have universal application, and we found that the most suitable solvent was a mixture of phenol and propionic anhydride, originally suggested by ELEK[7]. This mixture appeared to have an almost universal solvent action on organic compounds, and functioned satisfactorily for all compounds that we examined.

Hydriodic acid

Several workers have reported that the use of colourless hydriodic acid is essential for consistent results to be obtained. STEYERMARK[8], however, found that when reagent grade hydriodic acid (d = 1.7) was refluxed for several hours in a stream of carbon dioxide or nitrogen, satisfactory results were obtained, even if the reagent were almost black in colour. We obtained almost negligible blanks using M.A.R. hydriodic acid. Even when 10 mg of iodine were added to the hydriodic acid in the reaction flask, the reagent blank value did not increase. With the washing compartment filled with distilled water, only a trace of iodine was found under these exacting conditions. When 20 mg amounts of iodine were added to the reaction flask, a slight increase in the blank value was obtained, but this was still well within the permissible limits.

Table I summarizes these findings, the sample used being α-methyl-D-glucoside ($-OCH_3$ = 15.98%).

TABLE I

EFFECT OF IODINE ON REAGENT BLANK

Sample wt (mg)	*Iodine added (mg)*	*0.05N $Na_2S_2O_3$ (ml)*	*$-OCH_3$ found (%)*
—	—	0.06	—
—	10	0.06	—
—	20	0.12	—
19.201	10	11.97	15.82
19.182	20	11.89	15.81

When a small piece of tinfoil was placed in the reaction flask to promote even boiling in the reaction mixture, low results were obtained owing to reduction of the strength of the hydriodic acid following its reaction with the tin. More hydriodic acid had then to be added to maintain its effective concentration in the reaction mixture. Addition of two or three small platinum tetrahedra, which were unaffected by the hydriodic acid, gave a smooth boiling mixture. A drop of mercury[6] was equally effective, and as it reacted at the same time with any free iodine in the reaction mixture, it thus prevented the possible distillation of iodine vapours into the washing compartment. However, care had always to be taken not to introduce too large a drop of mercury, otherwise considerable frothing occurred in the neck of the reaction flask and the lower end of its attached condenser.

Wash liquids

Many wash liquids have been recommended for removing interfering gases and vapours from the alkyl iodide. Distilled water[9] proved efficient as a scrubber except when the compound contained sulphur, or when up to 10 mg of sodium sulphide were added to the flask. In this case some of the hydrogen sulphide produced in the reaction passed through the washing compartment into the receiver and consumed a small amount of bromine. When further amounts of bromine were added to allow for this consumption, results were satisfactory, although the blanks increased slightly. Similarly, satisfactory results were obtained using an aqueous suspension of red phosphorus in the washing compartment, although again some hydrogen sulphide escaped into the receiver. A solution consisting of a mixture of 5% cadmium sulphate and 5% sodium thiosulphate also proved efficient as a scrubber and retained any iodine and hydrogen sulphide produced in the reaction. No examination was made of the use of sodium thiosulphate solutions, because it has been known for many years from the studies of SLATER[19] that methyl iodide reacts with sodium thiosulphate in aqueous solution to form sodium methyl thiosulphate. The one-purpose wash liquid of FRANZEN, HEGEMANN AND DIESE[4], a 10% aqueous solution of sodium antimony tartrate, served to remove both iodine and hydrogen sulphide, and we found this to be the most convenient of all the wash liquids hitherto suggested. We recommend that this solution be used at all times as an additional refinement to the method, even though water itself was a sufficiently satisfactory wash liquid under the conditions we tried.

Absorption of alkyl iodide

The receiver used on the micro scale has a capacity of about 5 ml, but this volume of absorbent was inadequate for semimicro amounts of material. In order to cope with the quantity of sample used in semimicroanalysis, and also with compounds of high alkoxyl content, the most convenient volume of absorbent was found to be 10 ml. The necessity of using two receivers for the absorption of these larger amounts of alkyl iodide was avoided by increasing the length of the receiver and passing the alkyl iodide slowly through the absorbing solution by means of a glass spiral of fourteen turns. Satisfactory results were obtained in this way even when amounts of up to 60 mg of α-methyl-D-glucoside were decomposed.

Use of sodium and potassium acetates

The use of both sodium and potassium acetates in the determination was recommended by VIEBÖCK AND BRECHER[1], and, indeed, this procedure was adopted by several later workers. No explanation has ever been offered for this curious practice, but our results indicated that both acetates appeared to be equally effective in the absorption and the subsequent titration.

Blanks

Reagent blanks are normally carried out by omitting the sample and proceeding as in an actual determination. During our investigation, however, it was found that reagent blank values, determined in this way, were almost identical with those obtained from the direct titration of 10 ml aliquots of the absorbent. It was established that the principal blank source was the bromine, although the blank values obtained were negligibly low.

Determination of ethoxyl groups

Owing to the higher boiling point of ethyl iodide, a modification in the distillation procedure was necessary when organic compounds containing ethoxyl groups were analysed in the new apparatus. A longer heating period was required to complete the conversion to ethyl iodide, and during the last part of the distillation the water was removed from the condenser as recommended by Steyermark[11]. Table II lists a selection of the results obtained by research workers in this Department using the final method developed.

TABLE II

Compound	*% Alkoxyl*	
	Found	*Required*
Methyl-2-acetamido-2-deoxy-6-O-trityl-α-D-glucopyranoside	6.40	6.51
α-Methyl nigerfuranoside	8.19	8.35
β-Methyl nigerfuranoside	8.22	8.35
Methyl-2-acetamido-2-deoxy-4:6-O-benzylidene-α-D-glucosaminide	9.42	9.66
Methyl-2-acetamido-2-deoxy-β-D-glucopyranoside	13.13	13.28
2-Amino-2-deoxy-6-O-methyl-D-glucose hydrochloride	13.30	13.55
α-Methyl glucoside	15.95	15.98
Methyl-2-acetamido-2-deoxy-4-O-benzoyl-3-O-methyl-α-D-glucopyranoside	17.48	17.56
Vanillin	20.18	20.40
Methyl-2-acetamido-2-deoxy-3-O-methyl-β-D-glucosaminide	24.70	24.91
Phenacetin (as ethoxyl)	25.03	25.14
2-Amino-2-deoxy-3:6-di-O-methyl-D-glucose hydrochloride	25.59	25.54
2:3-Dimethyl-α-methyl glucoside	41.66	41.89
2:3:4-Trimethyl glucose	42.00	41.92
2:3:4:6-Tetramethyl glucose	52.25	52.52

APPARATUS

A line diagram of the complete assembled apparatus with the essential dimensions is shown in Fig. 1. The reaction flask and washing compartment are very similar in design to those described in British Standard 1428: Part CI : 1954 on the micro determination of alkoxyl groups, except that the gas inlet of the reaction flask is of uniform diameter and not tapered. The reaction flask, A, is of 5 ml capacity for use on a micro scale, and of 10 ml capacity on a semimicro scale, and is sealed to the water condenser, B, by a neck 2 cm in length. A B14 socket is attached to the top of the condenser. The B14 cone is sealed to the delivery tube, C, leading into the washing compartment, D. A solid glass spiral (9 spirals) is fused to the outside of the delivery tube. The receiver, F, is attached to the washing compartment by a glass tube, E, which leads successively through B10 and B14 joints to a delivery tube, G, to the outside of which a solid glass spiral (14 spirals) is fused. Two small side-arms, H_1 and H_2, are sealed into the apparatus. During an actual determination one of the side-arms is attached to a water pump, and by application of gentle suction, a current of air is drawn across the surface of the liquid in the receiver, removing bromine fumes which would otherwise escape into the atmosphere.

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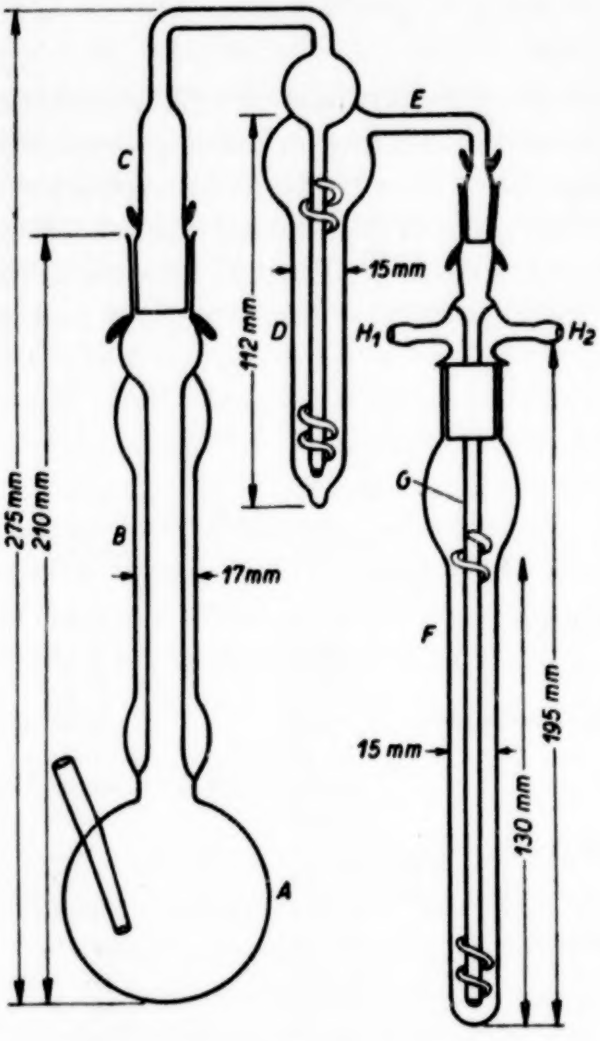

Fig. 1

METHOD

Reagents and materials

Carbon dioxide. Powder solid carbon dioxide and pack firmly into a vacuum flask fitted with a mercury valve release. Before use in a determination leave the freshly packed flask for several hours, preferably overnight, so that any occluded air is removed by displacement.

Hydriodic acid. Microanalytical Reagent Grade stabilized with hypophosphite. If several determinations are to be carried out, mix the contents of several ampoules (each 6 ml) and store in a stoppered brown reagent bottle which has previously been swept out with carbon dioxide. Run a blank on this stock of acid before each series of determinations.

Phenol. "AnalaR"Grade.

Propionic anhydride. Reagent Grade.

Bromine. "AnalaR"Grade.

Acetic acid — Sodium acetate solution. 10% solution of "AnalaR" sodium acetate trihydrate in "AnalaR" glacial acetic acid.

Sodium acetate solution. 25% solution of "AnalaR" sodium acetate trihydrate in distilled water.

Formic acid. 80-100% "AnalaR" Grade.

Sodium thiosulphate solutions. $0.02N$ for micro and $0.05N$ for semimicro determinations.

Starch solution. 0.5% solution.

Sulphuric acid. 10 % w/v.

Potassium iodide. "AnalaR" Grade.

Sodium antimony tartrate solution. 10% solution of Reagent grade sodium antimony tartrate in distilled water.

SEMIMICRO DETERMINATION

Clean the apparatus in warm chromic-sulphuric acid for 10 minutes, rinse well with tap water, then with distilled water, and dry in an oven at 120° C. Measure 3-4 ml of the sodium antimony tartrate solution into the spiral washing compartment and stopper the side arm. Place 10 ml of acetic acid-sodium acetate solution in the semimicro receiver and add 0.3 ml of "AnalaR" bromine. Lubricate the ground glass joints leading to the receiver with silicone grease and connect to the tube, E, sealed to the washing compartment. Attach one of the side-arms, H, to a water-pump and by gentle suction draw a slow stream of air across the top of the liquid in the receiver. Clamp the apparatus using retort stands, or preferably attach to a board by means of Terry clips.

Procedure

Weigh 15-20 mg of the sample in a platinum boat or glass cup, and slide down the condenser into the reaction flask. Lubricate the ground glass joint of the condenser with silicone grease and connect it to the washing compartment. Through the side-arm of the reaction flask add 0.5 ml of a solution of phenol in propionic anhydride (1 g in 10 drops of anhydride). Warm the mixture in order to dissolve the sample. Cool the reaction flask and add a small drop of mercury (or 2 or 3 platinum tetrahedra) followed by 5 ml of M.A.R. hydriodic acid through the side-arm by means of a finely tipped pipette. Connect the side-arm to the carbon dioxide supply and adjust the gas flow to give 1 bubble per second. Immediately place the small non-luminous flame of a mantled micro-burner about 6 inches below the reaction flask and bring the mixture slowly to the boil. Then raise the flame so that the refluxing vapours from the flask do not rise above half-way up the water condenser. Boil for 60 minutes; this is sufficient for the decomposition of most compounds, but certain tri- and tetra-methoxy compounds may require a heating period of 1½-3 hours. Ethoxy compounds require heating at least 1½ hours to complete the conversion of the ethoxy groups to ethyl iodide, and during the last 20 minutes of the reaction the water should be removed from the condenser.

When the heating is complete, disconnect the receiver and its spiral inlet tube. Rinse the B10 joint with a fine jet of distilled water and collect the washings in a 250 ml stoppered conical flask containing 5 ml of the aqueous sodium acetate solution. Transfer the contents of the receiver to this flask and rinse both the receiver and the spiral inlet tube with distilled water. The volume of the liquid in the flask should not exceed 40 ml. Add formic acid dropwise to the liquid in the flask until the excess of bromine is destroyed, making sure that any bromine in the vapour phase is completely removed by testing with methyl red indicator. Add 0.5 g of potassium iodide and 5 ml of sulphuric acid solution, stopper the flask, shake and then allow to stand for 5 minutes. Titrate the liberated iodine with $0.05N$ sodium thiosulphate solution using starch solution as indicator.

Carry out a blank determination on all reagents following the above procedure.

1 ml of $0.05N$ $Na_2S_2O_3$ = 0.2586 mg methoxyl
0.3755 mg ethoxyl

MICRO DETERMINATION

Fill the washing compartment as in the semimicro method; then place 5 ml of acetic acid-sodium acetate solution in the smaller micro receiver and add 0.2 ml of bromine. Connect up the apparatus as previously described.

Procedure

Weigh the sample (3-5 mg) in a platinum boat as before, transfer it to the flask and dissolve the sample in 3 small drops of the phenol-propionic anhydride mixture. Add 2 ml of hydriodic acid through the side-arm and proceed with the decomposition exactly as in the semimicro method. When the heating is complete, transfer the contents of the receiver and the washings to a 100 ml stoppered conical flask containing 3 ml of aqueous sodium acetate solution. The volume of the liquid in the flask should not exceed 40 ml. Destroy the excess of bromine with formic acid, add 0.5 g of potassium iodide and 5 ml of sulphuric acid and complete the titration of the liberated iodine with $0.02N$ sodium thiosulphate solution.

1 ml of $0.02N$ $Na_2S_2O_3$ = 0.1034 mg methoxyl
0.1502 mg ethoxyl.

SUMMARY

An examination has been made of the sources of error associated with the determination of alkoxyl groups. Several features of other methods have been incorporated in a simple apparatus, and a modified procedure is presented for both the micro and semimicro determination of methoxyl and ethoxyl groups.

RÉSUMÉ

On a examiné les sources d'erreurs possibles lors du dosage des groupements alcoxyle.

Un simple appareil est proposé tenant compte des caractéristiques d'autres méthodes. Un procédé modifié est décrit soit pour les microdosages, soit pour les semimicrodosages de groupements méthoxyle et éthoxyle.

ZUSAMMENFASSUNG

Die möglichen Fehlerquellen während der Bestimmung von Alkoxyl-Gruppen wurden geprüft.

Es wird ein einfacher Apparat vorgeschlagen, welcher auch Eigenschaften anderer Methoden Rechnung trägt. Ein modifiziertes Verfahren wird beschrieben so wohl für die Mikrobestimmungen als auch für die Semimikrobestimmungen von Methoxyl- und Ethoxyl-Gruppen.

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DETERMINATION OF THORIUM WITH ORGANIC REAGENTS: DIFFERENT METHODS USING *p*-AMINOSALICYLIC ACID

by

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INTRODUCTION

Thorium being the cheapest source of atomic energy, the need for a rapid and accurate method for its determination in trace concentration is now desirable. Nowadays, the use of volumetric procedures is becoming increasingly popular chiefly because the titration can be performed more rapidly and conveniently. METZGER AND ZONES[1] introduced the molybdate method for the volumetric determination of thorium. In its usual form, the method did not yield accurate results since it involved the use of diphenylcarbazide as an external indicator. Mention may be made of the oxalate method of GOOCH AND KOBAYASHI[2]. The oxinate method has also been employed with success for volumetric determination of thorium by BERG[3]. Recent work by the present authors[4] on the use of anthranilic acid for the volumetric determination of thorium has shown that in a suitable acid media, the thorium salt of anthranilic acid can be quantitatively brominated by a standard bromide-bromate solution and the excess of bromine can then be determined iodometrically.

During the course of the experimental work embodied in this report, it has been observed that *p*-aminosalicylic acid (PAS) gives a quantitative precipitation of thorium at a definite pH range between 4 to 5.6 and the composition of its thorium salt is $(C_7H_6O_3N)$-Th-$(OH)_3$, $3H_2O$, which has been found to be definite with slight variation in the number of associated water molecules. Thorium, thus, can be determined gravimetrically only by igniting the precipitate to thoria. Since the number of organic ligand associated with thorium in the precipitate is always fixed, the organic part of the molecule can easily be brominated by bromide-bromate solution and iodinated by iodine monochloride solution to yield dihalogenated products[5], and thus thorium can be determined by adopting such indirect volumetric methods also. The bromination method for the determination of thorium is based on the following reactions:

(1) $(C_7H_6O_3N)\text{-Th-}(OH)_3,\ 3H_2O + 4HCl \rightarrow Th^{+4} + 4Cl^- + C_7H_7O_3N + 6H_2O.$
(2) $KBrO_3 + 5KBr + 6HCl \rightarrow 3Br_2 + 6KCl + 3H_2O.$
(3) $C_7H_7O_3N + 2Br_2 \rightarrow C_7H_5O_3Br_2N + 2HBr.$
(4) $2KI + Br_2 \rightarrow 2KBr + I_2.$

From (1) and (3), it is evident that one atom of thorium is equivalent to $2Br_2$ and hence its equivalent weight becomes Th/4 or 58.03. Therefore, one atom of thorium is equivalent to 4 bromine atoms, *i.e.* to 4000 ml of N-bromate. Hence, 1 ml of N-$KBrO_3$ $\equiv$ 0.05803 g of thorium, the excess of bromine being determined iodometrically.

The iodination is carried out by standard ICl solution in glacial acetic acid and the reactions involved in the process are as follows:

(1) $(C_7H_6O_3N)\text{-Th-}(OH)_3{,}3H_2O + 4HCl \rightarrow Th^{+4} + 4Cl^- + C_7H_7O_3N + 6H_2O.$
(2) $C_7H_7O_3N + 2ICl \rightarrow C_7H_5O_3I_2N + 2HCl.$

From (1) and (2) it is seen that, one atom of thorium is equivalent to 2I and hence its equivalent weight is Th/2 or 116.06. Therefore, one atom of thorium is equivalent to 2 iodine atoms *i.e.* to 2000 ml, of *N* ICl. Hence, 1 ml *N* ICl $\equiv$ 0.1160 g of thorium, the excess of ICl being determined iodometrically.

The gravimetric procedure for the determination of thorium, has been adopted first in order to establish the suitability of the reagent for volumetric determinations.

EXPERIMENTAL

Reagents and chemicals

p-Aminosalicylic acid. B.D.H. reagent grade sample was recrystallized from water.

Thorium nitrate. (Merck's reagent.) A stock solution of thorium nitrate was prepared and estimated by standard oxalate method.

Iodine monochloride. ICl of sufficient purity was prepared as follows[6]:

Dry chlorine gas was led in at the surface of 1 mole of iodine in a 125 ml distilling flask while the flask was gently shaken. When 0.97 mole of chlorine had been introduced, the ICl was distilled in an ordinary distilling apparatus with a filter flask, protected from atmospheric moisture by a calcium chloride tube, as a receiver. The yield of ICl was 142 g. The product was preserved in a dry glass-stoppered bottle.

Potassium bromate. Finely powdered (Merck's A.R.) potassium bromate was dried for several hours at 110° C, and then cooled in a desiccator. A solution of $KBrO_3$ was prepared from this sample and standardized by titrating with pure arsenious oxide.

Indicator. The indicator used in bromination was a few drops of a solution, which was made up of 0.2 g indigo carmine and 0.2 g styphnic acid in 100 ml water.

Precipitation and analysis

A hot 2% solution of *p*-aminosalicylic acid in water, was slowly added to aliquot quantities of thorium nitrate solutions neutralized to congo red and in which 0.2 g of solid ammonium-acetate per 0.02 g of thorium present had already been added, until the precipitation was complete. A very pale yellow flocculent precipitate appeared at once, which was digested for about 5 minutes and filtered. The precipitate was washed repeatedly with boiling water, partially dried and then ignited to thoria to a constant weight. The results have been indicated in Table I.

TABLE I

DETERMINATION OF THORIUM USING PAS

No. of Expts.	*ThO_2 taken*	*ThO_2 found*	
		(A)	*(B)*
1	0.0880 g	0.0880 g	0.0881 g
2	0.0660	0.0661	0.0661
3	0.0440	0.0442	0.0441
4	0.0165	0.0164	0.0165
5	0.0082	0.0080	0.0081
6	0.0055	0.0053	0.0052

References p. 27

Effect of hydrogen ion concentration upon precipitation

In order to find out a suitable pH range for the effective precipitation of thorium, the determination was carried out by this reagent, as before, in solutions having different pH values. The results in Table II indicate that a pH range between 4 to 5.6 is suitable for the quantitative determination of thorium by *p*-aminosalicylic acid.

TABLE II

DETERMINATION OF THORIUM AT DIFFERENT pH VALUES

ThO_2 taken: 0.0440 g
Total volume of the solution = 45 ml

pH of the final solution	2.0	2.5	3.5	4.0	4.5	5.2	5.6	5.8
ThO_2 found in g	0.0091	0.0106	0.0210	0.0439	0.0441	0.0440	0.0441	0.0438

Influence of ammonium acetate

During preliminary studies, it has been observed that the addition of ammonium acetate is essential for the complete precipitation of thorium. Precipitate does not appear at all from a very dilute solution of thorium, if ammonium acetate is not present. A considerable excess of the reagent however, may bring down a slight precipitation of thorium from such solution, not containing any ammonium acetate. This electrolyte helps in the coagulation of the precipitate and thus renders filtration easier. The presence of a large excess of ammonium acetate, however, hinders its quantitative precipitation. The quantity of ammonium acetate required for the complete precipitation of a definite amount of thorium was therefore found out. Weighed amounts of solid ammonium acetate was added to thorium solutions rendered neutral to congo red, and thorium was precipitated as before. The results have been entered in Table III.

TABLE III

EFFECT OF AMMONIUM ACETATE UPON PRECIPITATION OF THORIUM

Expt. no.	*ThO_2 taken*	*Ammonium acetate added*	*ThO_2 found*	*Error*
1	0.0220 g	0.2 g	0.0220 g	±0.0000 g
2	0.0220	0.40	0.0219	−0.0001
3	0.0220	0.60	0.0221	+0.0001
4	0.0220	1.0	0.0220	±0.0000
5	0.0220	1.8	0.0221	+0.0001
6	0.0220	2.0	0.0216	−0.0004
7	0.0220	3.0	0.0194	−0.0026
8	0.0220	4.5	0.0192	−0.0028

It is evident from Table III that from 0.20 g to 1.8 g of ammonium acetate may be added for a solution having 0.0220 g of thoria, for the effective precipitation of thorium.

Composition of the thorium salt of p-aminosalicylic acid

The thorium precipitate in a sintered glass crucible (No. 3) was first washed several times with boiling water and then with hot alcohol, and dried in an electric oven at

105-110° C to a constant weight. Known quantities of the dried salt were ignited to the oxide. The results show that the thorium salt has the composition: $(C_7H_6O_3N)$-Th-$(OH)_3$, $3H_2O$, with slight variation in the associated water molecules, for which direct weighing of the salt is not possible.

VOLUMETRIC METHODS FOR THE DETERMINATION OF THORIUM

A. Bromination procedure

The thorium salt of PAS as precipitated by the previous method was filtered hot and washed several times as before in order to free it completely from the excess of the precipitant. It was dissolved in 1:1 HCl and quantitatively transferred to an iodine flask, shown in Fig. 1. A few drops of the prepared indicator and 0.5 to 1 g of pure KBr were added to the solution. It was then slowly titrated with standard $KBrO_3$ until colour became pure yellow indicating a slight excess of bromine in the solution. During bromination, the iodine-flask was stoppered and the cup filled with 10 ml of 20% KI solution to prevent escape of bromine. Then the titration was completed iodometrically. Thorium was then calculated from the amount of bromate used up, as 1 ml *N* $KBrO_3$ = 0.05803 g of thorium. The results of titration are shown in Table IV.

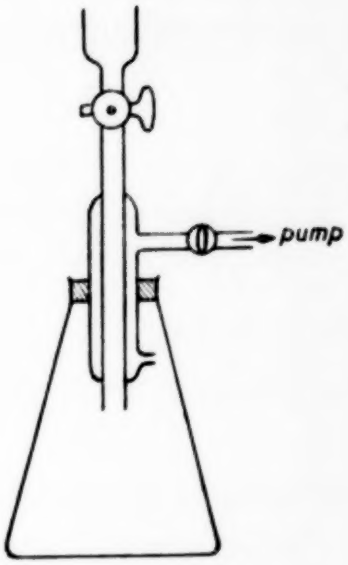

Fig. 1. Apparatus for bromination and iodination.

TABLE IV

DETERMINATION OF THORIUM BY BROMINATION

Expt. no.	*Thorium taken*	*Vol. of 0.0683N $KBrO_3$ used up*	*Thorium calculated*	*Difference*
1	0.1160 g	29.25 ml	0.1160	±0.0000 g
2	0.0967	24.40	0.0968	+0.0001
3	0.0774	19.50	0.0772	—0.0002
4	0.0580	14.65	0.0580	±0.0000
5	0.0387	9.80	0.0388	+0.0001
6	0.0193	4.90	0.0194	+0.0001

B. Iodination procedure

The Th-salt dissolved in HCl as before, in an iodine flask was cooled to 0° C, by immersing the flask in freezing mixture, to prevent the loss of iodine. A measured excess of standard ICl solution in glacial acetic acid was then added all at once, and was kept for 3 minutes in the dark for the completion of the iodination of the organic ligand. Then the solution was rapidly titrated by running in a standard Na-thiosulphate solution and adding starch towards the end. Thorium was then calculated from the amount of iodine used up, as 1 ml *N* ICl = 0.1160 g of Th. The results are given in Table V.

TABLE V

DETERMINATION OF THORIUM BY IODINATION

Expt. no.	*Thorium taken*	*Vol. of 0.1195N-ICl used up*	*Thorium calculated*	*Difference*
1.	0.1160 g	8.35 ml	0.1157 g	—0.0003 g
2.	0.0967	7.0	0.0970	+0.0003
3.	0.0774	5.6	0.0776	+0.0002
4.	0.0580	4.2	0.0582	+0.0002
5.	0.0387	2.8	0.0388	+0.0001
6.	0.0193	1.35	0.0187	—0.0006

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SUMMARY

p-Aminosalicylic acid (PAS) can be successfully utilized as a reagent for gravimetric and volumetric determination of thorium. A quantitative precipitate of thorium is obtained by adding a hot 2% solution of PAS, in the presence of a little ammonium acetate at a pH range between 4 and 5.6. The thorium salt filters, washes and ignites readily. Thorium content of the salt can be determined directly by ignition to thoria, and indirectly by the quantitative bromination of the organic ligand with bromide-bromate mixture or by iodination with iodine monochloride in glacial acetic acid solution at 0° C. The processes give comparable results.

RÉSUMÉ

L'acide *p*-aminosalicylique (PAS) peut être utilisé avantageusement comme réactif pour les dosages volumétriques et gravimétriques du thorium. Une précipitation quantitative du thorium est obtenue par addition d'une solution bouillante de PAS à 2%, en présence d'un peu d'acétate d'ammonium à un pH compris entre 4 et 5.6. Ce sel de thorium se filtre, se lave et se calcine rapidement. La teneur en thorium dans ce composé peut être déterminée directement par calcination en oxyde de thorium, ou indirectement par bromuration de la partie organique par le mélange bromate-bromure ou encore par ioduration au moyen du monochlorure d'iode dans l'acide acétique glacial à 0° C. Tous ces procédés donnent des résultats comparables.

ZUSAMMENFASSUNG

Die *p*-Aminosalicylsäure (PAS) kann mit Erfolg als Reaktiv für die volumetrischen und gravimetrischen Bestimmungen für das Thorium gebraucht werden. Man erhält einen quantitativen Niederschlag des Thoriums durch Zugabe einer siedenden Lösung, die 2% (PAS) enthält in Gegenwart von wenig Ammoniumacetat, bei pH Werten zwischen 4 und 5.6.

Dieses Thoriumsalz kann rasch filtriert, gewaschen und kalziniert werden. Der Gehalt an Thorium in dieser Zusammensetzung kann direkt bestimmt werden, indem man es zu Thoriumoxyd kalziniert, oder indirekt, indem man den organischen Teil bromiert mit einer Bromid-bromat Mischung, oder sogar indem man iodiert mit Hilfe von Jodmonochlorid in Eisessig bei 0° C. Alle diese Verfahren geben vergleichbare Resultate.

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ESTIMATION OF METALS AS SULPHIDES
IV. ATMOSPHERIC OXIDATION OF ALKALI SULPHIDES

by

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In earlier publications[1-6] from these laboratories it has been shown that many elements can be estimated as sulphides, either by precipitating the sulphides directly with alkali sulphides, or by decomposing their thiosalts with excess of hydrochloric or acetic acid. The sulphide precipitate can be weighed after it has been washed with water alone, or with water, alcohol and ether successively.

It was possible to apply this simple method to many elements, chiefly because the precipitates of sulphides produced by using the special alkali sulphide reagent were free from sulphur, and could be weighed directly without any further treatment. When the alkali sulphide reagent is prepared by passing hydrogen sulphide into alkali solution at ordinary temperatures for an indefinite period, it contains varying amounts of sulphur[7] dissolved in it. This sulphur is precipitated along with the insoluble sulphide in varying amounts, and accounts for the indefiniteness of the composition of the precipitate. In some cases, such as Volhard's method[8] for estimating mercury as sulphide, it is possible to remove this sulphur by washing with a solvent like carbon disulphide. But with other sulphides it is not possible to remove the free sulphur in this manner, and the precipitate cannot therefore be weighed directly[9].

In the earlier stages of these investigations it was found in a general way that the manner in which the alkali sulphide reagent was prepared determined its efficacy in producing a pure precipitate of the insoluble sulphide. If the reagent was prepared at ordinary temperatures, and exposed for some time to the atmosphere, the precipitate of sulphide produced by it was contaminated with sulphur and gave discordant results. On the other hand, if the alkali sulphide reagent was prepared by passing hydrogen sulphide into a nearly ice-cold alkali solution, the precipitate of sulphide produced by it, either directly or by decomposing the thiosalt, was pure and could be weighed directly for the estimation of the element. In the estimation of elements as sulphides, the alkali sulphide reagent was therefore always prepared freshly by passing hydrogen sulphide into the alkali solution at a temperature below 5° C.

In view of the importance of preparing the alkali sulphide reagent at a low temperature for obtaining pure precipitates of sulphides, it was considered necessary to investigate in greater detail the oxidation of alkali sulphides by atmospheric oxygen. It is only when the behaviour of these alkali sulphides has been studied in sufficient detail, under different conditions of temperature, that one can prepare a reagent of the right composition and get precipitates of uniform composition with any degree of certainty. Besides temperature, the time for which hydrogen sulphide is passed into the alkali solution also affects the oxidation of the reagent. It was found that by increasing this period, the rate of oxidation of the sulphide reagent also increases progressively, and the precipitation of sulphur on acidification takes place in a shorter time. Some salts of heavy metals like nickel and manganese are also known to promote aerial oxidation of alkali sulphide solutions catalytically[10,11] but this aspect of the problem was not studied in the present investigation.

EXPERIMENTAL

To determine the effect of temperature on the oxidation of the alkali sulphide reagent, 150 ml of the alkali hydroxide solutions of different concentrations were taken in a reagent bottle which was placed in a bath kept at different constant temperatures. Hydrogen sulphide was passed into the solution for a fixed time. 5 ml of the reagent was then taken out of the reagent bottle and treated with excess of hydrochloric acid at regular intervals of time. The beginning of oxidation was indicated by the formation of a precipitate of sulphur. The time after which the precipitate appeared on acidification was noted in each case. The following tables give the results of the different experiments, and show how the oxidation of the alkali sulphide reagent is affected by temperature and the time for which hydrogen sulphide is passed in the solution.

TABLE I

OXIDATION OF AMMONIUM SULPHIDE REAGENT AT DIFFERENT TEMPERATURES. HYDROGEN SULPHIDE PASSED FOR 2 MINUTES

Conc. of $(NH_4)_2S$	*Temp. in °C*	*Time up to which there is no oxidation (min)*	
		Stoppered bottle	*Unstoppered bottle*
1*N*	5	360	300
1*N*	10	90	60
1*N*	15	60	60
1*N*	20	0	0
15*N*	5	360	300
15*N*	10	90	60
15*N*	15	60	60
15*N*	20	0	0

TABLE II

OXIDATION OF AMMONIUM SULPHIDE REAGENT AT DIFFERENT TEMPERATURES. HYDROGEN SULPHIDE PASSED FOR 4 MINUTES

Conc. of $(NH_4)_2S$	*Temp. in °C*	*Time up to which there is no oxidation (min)*	
		Stoppered bottle	*Unstoppered bottle*
1*N*	5	300	240
1*N*	10	75	60
1*N*	15	45	30
1*N*	10	0	0
15*N*	5	300	240
15*N*	10	75	60
15*N*	15	45	30
15*N*	20	0	0

TABLE III

OXIDATION OF SODIUM SULPHIDE REAGENT AT DIFFERENT TEMPERATURES. HYDROGEN SULPHIDE PASSED FOR 2 MINUTES

Conc. of Na_2S	*Temp. in °C*	*Time up to which there is no oxidation (min)*	
		Stoppered bottle	*Unstoppered bottle*
1*N*	5	180	120
1*N*	10	45	45
1*N*	15	30	30
1*N*	20	0	0
2*N*	5	180	120
2*N*	10	45	45
2*N*	15	30	30
2*N*	20	0	0

TABLE IV

OXIDATION OF SODIUM SULPHIDE REAGENT AT DIFFERENT TEMPERATURES. HYDROGEN SULPHIDE PASSED FOR 4 MINUTES

Conc. of Na_2S	*Temp. in °C*	*Time up to which there is no oxidation (min)*	
		Stoppered bottle	*Unstoppered bottle*
1*N*	5	120	90
1*N*	10	30	30
1*N*	15	15	10
1*N*	20	0	0
2*N*	5	120	90
2*N*	10	30	30
2*N*	15	15	10
2*N*	20	0	0

Note: — The time zero minute for oxidation in the above tables indicates that a precipitate of sulphur is obtained on addition of hydrochloric acid immediately after passing hydrogen sulphide.

From the results obtained the following facts are apparent.

(1) The oxidation of the alkali sulphide solution is very susceptible to changes of temperature and increases markedly with rise in temperature. The important point to note is that there is no appreciable oxidation below 5° C, no oxidation being detected even after keeping the reagent in a refrigerator for 96 hours.

(2) If the hydrogen sulphide is passed for a longer period precipitation of sulphur, which gives an indication of oxidation, takes place after a shorter interval.

(3) The oxidation is of course increased by keeping the bottle unstoppered.

(4) The sodium sulphide reagent is oxidized more quickly than the ammonium sulphide reagent, even though the yellow colour develops more slowly in the former.

In the previous set of experiments only the time during which no oxidation could be detected was noted. A series of experiments was also performed to measure the quantity of sulphur precipitated. Measured portions of the alkali solutions which had been treated with hydrogen sulphide for two minutes and kept at a constant temperature in a stoppered bottle were acidified with hydrochloric acid after different periods of time and the sulphur precipitated was weighed. As expected, the amount of sulphur precipitated was found to increase with the passage of time. Some idea of the quantity of sulphur precipitated may be obtained from the Table V.

TABLE V

DETERMINATION OF SULPHUR IN THE ALKALI SULPHIDE REAGENT AT 25° C

Reagent	*Volume of reagent taken (ml)*	*Time after which sulphur is ppted (h)*	*Wt of sulphur ppted in g*
$2N$ Na_2S	25	0	0.0010
	25	18	0.0022
	25	24	0.0030
	25	42	0.0050
$15N$ $(NH_4)_2S$	25	0	0.0010
	25	18	0.0014
	25	24	0.0016
	25	42	0.0020

From the above experiments also it is seen that the sodium sulphide is oxidized more rapidly than the ammonium sulphide. This may be due to the protective action of ammonia vapour over the ammonium sulphide solution. Although sodium sulphide is oxidized far more rapidly than ammonium sulphide, its use in gravimetric analysis is possible owing to the fact that at low temperatures (below 5° C) practically no oxidation takes place for a long time, and the sulphide precipitates produced by it are therefore free from sulphur.

SUMMARY

The atmospheric oxidation of sodium and ammonium sulphide reagents has been studied. It has been shown that if the reagents are prepared by passing hydrogen sulphide from 2-4 minutes in alkali hydroxide solutions at a temperature below 5° C they remain unoxidized for a considerable time, and the sulphide precipitates produced by them in gravimetric analysis are therefore free from sulphur.

RÉSUMÉ

L'oxydation atmosphérique des sulfures de sodium et d'ammonium a été étudiée. Il est démontré que lorsque ces réactifs sont préparés par passage de l'hydrogène sulfuré, pendant 2-4 minutes, dans des solutions d'hydroxydes alcalins à une température inférieure à 5° C, ils ne s'oxydent pas à l'air pendant un temps relativement long; les précipités de sulfures obtenus en analyse gravimétrique, au moyen des réactifs ainsi préparés, sont exempts de soufre.

ZUSAMMENFASSUNG

Die Oxydation an der Luft von Natriumsulfiden und Ammonium wurde untersucht. Es wurde gezeigt, dass sich diese Reaktive während einer ziemlich langen Zeit an der Luft nicht oxydieren, falls sie durch Einleiten von Schwefelwasserstoff in Alkalihydroxydlösungen bei einer Temperatur unter 5° C während 2-4 Minuten, zubereitet worden sind.

Bei der gravimetrischen Analyse sind die Niederschläge, welche mit dem so zubereiteten Reaktiv erhalten worden, frei von Schwefel.

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SUR LA STABILITÉ THERMIQUE DES ÉTALONS ANALYTIQUES. I

par

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Au cours des sept dernières années, nous avons rendu compte dans cette revue et dans un livre récent[1] du sort des précipités formés en vue d'effectuer des gravimétries minérales. Entre temps, nous avons été conduits à tracer sur l'une ou l'autre de nos thermobalances, des courbes de thermolyse relatives à des produits qui ne sont pas, en général, des précipités destinés à être pesés, mais des substances très diverses de nature, qui sont destinées à servir d'étalons. Ce mot est pris dans une acception très large puisqu'il désigne, à notre sens, les substances de composition suffisamment certaine pour établir le titre d'une liqueur, celles qui servent à construire des tampons et, enfin, des étalons d'oxydo-réduction, des étalons aussi pour le réactif de Karl Fischer en aquamétrie et des réactifs pour faire les liqueurs de comparaison en colorimétrie ou spectrocolorimétrie. Le plus souvent, nous avons effectué ces chauffages pour certains de nos correspondants, en vue de les éclairer sur leurs recherches de l'époque. Comme la plupart de ces travaux risquent d'être perdus, nous avons décidé de les rassembler dans une série de mémoires, afin qu'ils puissent servir à tous les chimistes analystes.

Le plan suivi est tout simplement l'ordre chronologique. Les corps présentés dans cette première série n'ont aucun lien apparent. Ils ont donné lieu et donnent encore lieu à des controverses. Nous pensons donc qu'il est indispensable d'apporter notre contribution à ce sujet. Les substances étudiées sont: le carbonate de sodium, l'hydrogéno-carbonate de sodium, l'acétate de sodium, le borax, le phosphate disodique, le phosphate trisodique, le sel de Seignette, l'oxalate d'ammonium, l'hydrogénophtalate de potassium, le carbonate de lithium, le chlorure de baryum et le bichromate de potassium.

Carbonate de sodium

Ce sel est proposé depuis longtemps pour l'établissement des liqueurs titrées acides. Il a ses partisans et ses détracteurs. Déjà, dans une note rapide[2], nous avions indiqué sa grande stabilité thermique. Nous avons repris ce travail en profitant des derniers perfectionnements des thermobalances et en effectuant le chauffage d'une manière reproductible, de façon que l'élévation de température soit rigoureusement proportionnelle au temps: dans le cas présent, 250° par heure. Les prises vont de 200 à 500 mg. Nous avons effectué deux groupes de courbes avec des sels de provenance R.P. Le premier groupe montre que le carbonate est véritablement sec lorsqu'on le sort d'un flacon neuf. La courbe inscrite est horizontale jusqu'à 840°, au voisinage du point de fusion; il se produit alors une décomposition brusque qui se prolonge jusque vers 1000°. Pour un poids initial de sel sec de 559.4 mg, la perte à cette température s'élève à 23.0 mg.

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* Avec la collaboration technique de Mlles COLETTE WADIER ET YVETTE SERVIGNE.

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Le second groupe d'expériences porte sur le même produit auquel on ajoute intentionnellement un peu d'eau pour savoir à quelle température exacte celle-ci a ensuite disparu. La courbe de la Fig. 1 nous renseigne à cet égard. L'eau est complètement chassée à partir de 76° jusqu'à 100°; donc, pratiquement, après ouverture d'un flacon, on pourra être sûr que l'humidité sera évacuée et que le sel servira en vue d'une pesée si on le maintient pendant quelque temps entre 100 et 840°. Tout récemment, LASSIEUR[3] a discuté dans deux articles, de la stabilité et de l'emploi du carbonate de sodium comme étalon pour acidimétrie. Il critique, en particul er, notre premier travail dans lequel nous avons donné comme température maximum 980°. Celle-ci, comme nous l'avons dit, est assurément trop élevée et nous conseillons de ne pas dépasser 840°. Ensuite, il fait remarquer que CHARLOT ET BÉZIER[4] indiquent une perte de gaz carbonique au-dessus de 300°. L'examen attentif de nos courbes de thermolyse, confirme que ce dégagement, s'il existe, ne peut troubler en aucune facon l'établissement d'une liqueur titrée acide dans les conditions actuelles de préparation. LASSIEUR critique ensuite une étude de DESJOBERT ET PETEK, parue dans cette revue. Nous n'avons pas cherché, comme l'indiquent ces auteurs, a combler une lacune du travail de LASSIEUR et nous restons sur les conclusions suivantes qui nous paraissent être d'accord avec celles de ce dernier: (1) le carbonate de sodium pur pour analyses, issu d'un flacon neuf, peut être employé tel quel, (2) si le flacon a été ouvert plusieurs fois, il est recommandé de maintenir le sel pendant $^1/_4$ d'heure entre 100 et 840°, (3) le carbonate de sodium ne change pas de poids entre ces deux températures: nous voulons dire par là, qu'une perte de 1/10 mg n'est pas observable par inscription à la thermobalance pour un poids de matière compris entre 200 et 500 mg.

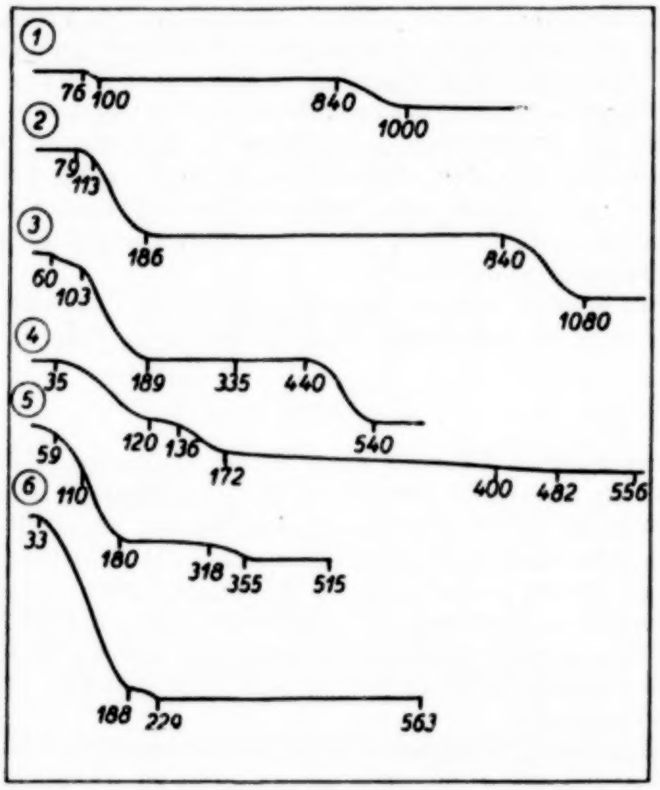

Fig. 1. Courbes de thermolyse. (1) Carbonate de sodium humide. (2) Hydrogénocarbonate de sodium. (3) Acétate de sodium. (4) Borax. (5) Phosphate disodique. (6) Phosphate trisodique.

En vue de l'identification rapide d'un carbonate de provenance inconnue ou douteuse, nous avons enregistré avec les mêmes poudres nous ayant servi dans le travail ci-dessus, le spectre d'absorption infrarouge, entre 6 et 15mμ sur un appareil Perkin-Elmer 12C équipé au chlorure de sodium. La cuve a été réalisée par la méthode décrite très souvent par LECOMTE ET DUVAL. Le carbonate utilisé ne renferme pas trace décelable de bicarbonate (absence de la bande 839 cm^{-1}). Voici les bandes qu'accuse le spectre: 685(aF), 693(aF), 701(aF), 851(aF), 869(TF), 881(TF), 903(f), 1041(?), 1072(f), 1440(TF). Ces valeurs s'accordent assez bien avec C. DUVAL, R. DUVAL, LECOMTE[6], puis plus tard avec MILLER ET WILKINS[7].

Hydrogénocarbonate de sodium

Nous avons chauffé un hydrogénocarbonate de sodium commercial, 256 mg environ à la vitesse de chauffe de 300° par heure. Le poids se maintient constant jusqu'à 79°, température à laquelle

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commence une dissociation lente et vers 113° le corps a perdu environ 4 mg. On voit alors la courbe changer de direction et la dissociation en carbonate est complète, en creuset ouvert et libre évacuation du gaz carbonique, à 186°; après quoi, commence le palier horizontal du carbonate de sodium comme sur la courbe 1 avec commencement de dissociation à 840° (courbe 2). Ce sel peut donc servir pour l'établissement d'une liqueur titrée et l'examen de son spectre infrarouge confirme sa pureté: 696(F), 839(TF), 999(F), 1032(aF), 1045(aF), 1287(f), 1402(f), 1460(F). Remarquons bien que les bandes très fortes qu'il donne à 696, 838 et à 999 cm^{-1}, ne se retrouvent pas dans le spectre du carbonate, ce qui est une nouvelle preuve de sa pureté.

Acétate de sodium

(corps pesé pour faire des liqueurs tampons)

La courbe de thermolyse de l'acétate de sodium indique que le produit commercial vendu sous le nom de trihydrate, perd de l'eau dès la température ordinaire. Dans aucun de nos essais, il ne contenait rigoureusement trois molécules d'eau, mais seulement entre 2.77 et 2.80 H_2O. La déshydratation est terminée suivant la vitesse de chauffe, entre 155 et 170°. Onobserve nettement deux points d'inflexion, l'un vers 55°, l'autre vers 95° (courbe 3). Si donc, on veut faire une liqueur titrée avec ce corps, il faut le prendre anhydre, c'est-à-dire, le peser après l'avoir maintenu pendant un certain temps entre 170 et 440°. Après cette température commence la destruction de l'acétate, opération qui semble terminée à 540°; après quoi, commence le palier horizontal du carbonate de sodium qui peut être parfois souillé de charbon.

Le spectre infrarouge d'un produit obtenu suivant le palier de l'acétate anhydre, accuse les bandes suivantes: 891(tf), 925(F), 1010 et 1046(TF), 1157(tf), 1262(tf), 1385(aF), 1460(F), 1589(TF).

Borax

Pour le borax, nous nous sommes adressés à un produit commercial, cristallisé, chauffé à raison de 150° par heure. Cet hydrate est stable jusqu'à 35-38°; il perd alors lentement la moitié de son eau jusque vers 108° où apparaît un palier oblique ou simplement un point d'inflexion. Après quoi, le départ d'eau reprend à peu près régulièrement jusqu'à 172° et la dernière molécule est très solidement attachée. Il faut chauffer au moins jusqu'à 500 ou même 525° pour obtenir le poids constant du sel anhydre. Le produit de départ ne contient pas rigoureusement 10 H_2O mais 9.45. Un autre échantillon recristallisé à partir du produit anhydre, ne renferme que 9.1 H_2O, mais l'allure de la courbe de déshydratation reste la même (courbe 4). On ne peut donc peser ce corps pour faire des tampons comme décahydrate avec certitude.

Voici maintenant les longueurs d'onde des spectres infrarouges relatifs au produit anhydre obtenu dans les limites indiquées ci-dessus: 1069 (très large), 1380(F), 1470(F).

Phosphate disodique

Le produit commercial retiré des bouteilles ne contient jamais 12 molécules d'eau de cristallisation mais un nombre voisin de 7. Celui qui nous a servi pour cette étude contient 6.7 H_2O. La déshydratation commence dès la température ordinaire; elle semble achevée, en chauffant à 300° par heure, à 180° où commence le palier bien horizontal du phosphate disodique anhydre. Ce sel est stable pendant au moins 100°. On sait qu'à ce moment, entre deux molécules, il perd une nouvelle molécule d'eau qui le conduit au-dessus de 355° au pyrophosphate de sodium (courbe 5). Si donc, en préparant une solution tampon, on préfère s'adresser au sel anhydre plutôt qu'aux produits commerciaux de teneur variable, il faudra maintenir le sel préalablement entre 180 et 280°.

Voici les longueurs d'onde relatives à ce produit anhydre: 861(TF), 946(TF), (peut-être contenant une bande faible à 940), 1079(TF), 1157(TF), 1380(TF), 1471(TF). Ces chiffres sont en accord avec un mémoire précédent de LECOMTE ET DUVAL[8].

Phosphate trisodique

Nous avons pris un produit commercial retiré d'un flacon qui avait été plusieurs fois ouvert, d'une part, et des cristaux obtenus en neutralisant exactement de l'acide phosphorique par la soude, d'autre part. Les chauffages se sont effectués à 300° par heure. Le premier de ces corps accuse 2.3 molécules d'eau, le second 10.4. C'est donc probablement un mélange de 10 et de 12 H_2O ou de 12 et de 7 H_2O. De plus, il est difficile d'empêcher ces produits de se carbonater. La courbe de thermolyse (courbe 6) indique un palier horizontal pour le phosphate trisodique à partir de 230°. Naturellement, en examinant cette courbe au voisinage de 840°, on verra si elle possède un léger ressaut correspondant à la dissociation du carbonate de sodium éventuellement présent. Là encore, pour faire une liqueur titrée pour tampon, il sera beaucoup plus sûr de s'adresser au sel anhydre. Le spectre

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infrarouge du produit anhydre contient les bandes suivantes: 802 (tf), 881 (f) (due au carbonate de sodium), 937(f), 1014(tf), 1032(tf), 1050(tf), 1069(tf), (due au carbonate de sodium), 1385(F), 1495(TF). On peut considérer comme sûres 1495 et la triple bande 1014, 1032, 1050, (parfois en une seule). Il sera donc possible grâce à la fréquence relative au groupement CO_3 de voir si le produit utilisé est carbonaté.

Sel de Seignette

La courbe de thermolyse relative au tartrate de sodium et de potassium est décroissante depuis 40°; elle se montre très accidentée mais ne présente aucun palier horizontal. Comme il n'y a aucun point de repère de poids constant sur la courbe, il nous paraît difficile de recommander ce sel pour une pesée précise. On est obligé d'admettre qu'il contient bien rigoureusement 4 molécules d'eau (courbe 7). Le sel ne doit pas être séché au-dessus de 40°; il perd de l'eau aussitôt.

Nous ne reproduisons pas le spectre d'absorption infrarouge déjà donné dans un mémoire précédent[9].

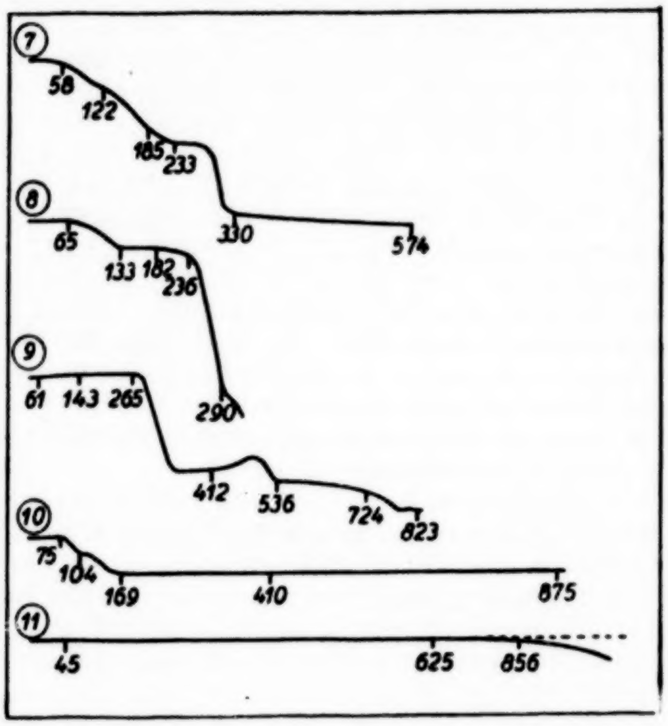

Fig. 2. Courbes de thermolyse. (7) Sel de Seignette. (8) Oxalate d'ammonium. (9) Hydrogénophtalate de potassium. (10) Chlorure de baryum. (11) Bichromate de potassium.

Oxalate d'ammonium

L'oxalate d'ammonium monohydraté que nous avons utilisé est stable jusque vers 65° en chauffage à 300° par heure. Il perd sa molécule d'eau entre 68 et 133° et se montre anhydre et stable jusqu'à 182° (courbe 8). Commence alors la formation d'oxamide jusqu'à 236°, puis, le cyanogène se dégage très rapidement jusque vers 290°. Notre produit de départ ne contenait en réalité que 0.95 H_2O. Là encore, dans le cas d'un dosage précis, il sera préférable d'utiliser le sel anhydre. Voici les bandes du spectre infrarouge relatif à celui-ci: 772(F), 779(f), 810(tf), 863(tf), 891(tf), 1079(tf), 1310(F), 1455(TF), 1600(TF), 1700(aF).

Hydrogénophtalate de potassium

Nous avions déjà étudié le comportement de ce sel en 1951[10] et nous avons indiqué qu'il conserve un poids constant au moins jusqu'à 240° lorsqu'il est chauffé à une vitesse de 150° par heure. Depuis cette date, CALEY ET BRUNDIN[11] ont publié une note en désaccord avec la nôtre et ils prétendent que ce corps, très utilisé comme étalon, perd du poids à 145°. Nous avons repris ces expériences et tracé les isothermes de 150°, 160° et 170° pendant trois heures. *On n'observe aucune perte de poids.* En chauffage continu, linéairement croissant, nous trouvons que la décomposition commence à 240° pour un chauffage de 150° par heure et 236° pour 300° par heure. *En aucun cas, nous n'avons observé de perte à* 145° comme l'ont rapporté CALEY ET BRUNDIN, sur des produits R.A.L., pris dans des flacons neufs (courbe 9). Ce composé est toujours anhydre et bien sec. Voici les bandes que présente son spectre infrarouge: 676(aF), 693(aF), 766(F), 773(f), 794(aF), 815(F), 853(F), 888(m), 963(f), 995(f), 1041(tf), 1085(f), 1099(f), 1150-1157(aF), 1163(f), 1271-1287(TF), 1380(TF), 1471(TF), 1560(F).

Carbonate de lithium

Le carbonate de lithium a été proposé comme tampon de pH par SOUCHAY ET SCHAAL[12]. Ce sel chauffé dès la température ordinaire jusqu'à 428° nous a donné une droite. Son spectre infrarouge ne présente que des bandes relatives à l'ion CO_3, savoir: 849(f), 866(TF), 921(tf), 975(tf), 1090(aF), 1157(tf), 1390(aF), 1475(F).

Chlorure de baryum

Le chlorure de baryum bihydraté a été proposé à plusieurs reprises comme étalon en aquamétrie. Cependant, différentes personnes ont eu des mécomptes en se servant de ce sel paraissant bien sec et bien cristallisé, pour étalonner la liqueur de Karl Fischer. De plus, il a été proposé comme forme de pesée dans une publication récente de la Commission de l'énergie atomique américaine (A.C.E.D. 2738). Nous avons utilisé trois produits commerciaux, a savoir: Prolabo, flacon neuf; Prolabo, flacon plusieurs fois ouvert; OSI, flacon plusieurs fois ouvert et nous avons fait recristalliser dans l'eau, du produit anhydre, en abandonnant le cristallisoir à la température ordinaire. Les courbes de thermolyse enregistrées sur ces produits paraissent très semblables; elles partent horizontalement et les corps commencent à perdre de l'eau vers 60° avec une vitesse de chauffage de 300° par heure et un poids de substance allant de 180 à 250 mg (courbe 10). Après quoi, on observe un court palier horizontal vers 104-107° correspondant au monohydrate, puis le chlorure de baryum anhydre se manifeste par un palier horizontal à partir de 150°, poids qui se maintient au moins jusqu'à 875°. Le calcul nous montre cependant que tous ces corps ont des compositions différentes du point de vue de leur teneur en eau. Ils nous donnent respectivement: 1.98 H_2O, 0.8 H_2O, 1.8 H_2O, et 1.95 H_2O. Les conclusions qui s'imposent sont alors les suivantes: le chlorure de baryum bihydraté n'est pas stable; c'est un mélange de mono- et de dihydrate; on ne peut l'employer comme étalon sûr en aquamétrie et comme forme de pesée en gravimétrie. En vue de faire une liqueur titrée pour ampérométrie, dosage des sulfates, *etc.*, il est préférable de déshydrater le sel de composition douteuse, que l'on a en mains, en le portant au voisinage de 160°.

Le chlorure de baryum est transparent dans la région 6-15 μ, mais nous avons précédemment[13] enregistré son spectre à l'état hydraté, avec un prisme de fluorure de lithium. On observe trois bandes assez fortes; deux d'entre elles à 3230 (F) et 3300 (m) concernent des molécules d'eau moyennement liées. D'autre part, une bande à 3568 (F) est relative à une eau beaucoup moins liée mais, en aucun cas, on ne rencontre dans ce sel d'eau monomère ou zéolithique. Précisons bien que ces trois bandes sont dues à l'eau seule, puisque le chlorure de baryum est transparent, et non aux groupements OH.

Bichromate de potassium

Ce sel est toujours anhydre et bien sec quel que soit l'échantillon prélevé. Sa thermolyse est extrêmement simple et se traduit par une droite horizontale (courbe 11). La température exacte du commencement de la dissociation est difficile à déterminer car celle-ci démarre lentement entre 625 et 650°; elle ne commence à devenir sensible qu'à 700° (perte de 1/100 environ).

Le spectre infrarouge du bichromate, comme d'ailleurs celui de tous les corps contenant le groupement X_2O_7 est très compliqué et difficile à interpréter. On y relève les bandes suivantes:
759(f), 765(f), 798-800 (bande double, f), 885(F); 891(f), 903(F), 909(f), 924(aF), 935(aF), 946(F), 954(m), 968(m), 1380(F), 1470(TF), qui ne permettent pas de confirmer l'une ou l'autre des structures proposées jusqu'ici pour l'ion $Cr_2O_7^{-2}$.

RÉSUMÉ

Les auteurs ont étudié la stabilité thermique de 12 substances servant comme étalon en chimie analytique et enregistré leur spectre infrarouge. Ils observent de grandes irrégularités pour la teneur en eau des sels hydratés et notamment dans le cas du chlorure de baryum. Ils recommandent, en général, la substance anhydre et fournissent la température minimum de son obtention.

SUMMARY

The authors have studied the thermal stability of 12 substances used as standards in analytical chemistry and have recorded their infra-red spectra. They observe large irregularities in the water content of hydrated salts, especially in the case of barium chloride. They recommend in general the anhydrous substance and give the minimum temperature necessary for obtaining it.

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ZUSAMMENFASSUNG

Die Autoren haben die thermische Stabilität von 12 Substanzen untersucht, welche als Vergleichslösungen in der analytischen Chemie dienen und haben ihre Ultrarotspektren aufgenommen. Sie beobachten grosse Unregelmässigkeiten in Bezug auf den Gehalt an Wasser in hydratisierten Salzen und zwar speziel im Falle von Bariumchlorid. Sie empfehlen im allgemeinen die wasserfreie Substanz und geben die minimale Temperatur an, welche notwendig ist, um sie in dieser Form zu erhalten.

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ÜBER DIE ABTRENNUNG KLEINER PHOSPHORSÄUREMENGEN VON EISEN UND VANADIN DURCH VERTEILUNG UND DURCH IONENAUSTAUSCH *

von

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Bei dem Versuch, den geringen Phosphorgehalt von Ferrovanadin nach der Methode von IWANTSCHEFF UND MEUWSEN[1] (Fällung als Molybdatophosphat nach Reduktion des Vanadins mit Hydrazin) zu bestimmen, erhielten wir in Übereinstimmung mit HOLDER[2] wesentlich zu niedrige Werte. Auf der Suche nach einem anderen Wege schien es uns am sichersten, das Vanadin vor der Bestimmung des Phosphors abzutrennen. Wir prüften zwei Verfahren: die Extraktion der Molybdatophosphorsäure aus wässriger Lösung mit Äthylacetat und die Bindung des Vanadins als VO^{+2} an einem Kationenaustauscher. Beide Wege führen zum Ziele und trennen zugleich das Eisen und weitere Elemente ab. Das Ionenaustauschverfahren ist für die analytische Praxis besser geeignet. Wir beschreiben im folgenden aber auch unsere Versuche über das Verteilungsverfahren, weil die dabei gewonnenen Ergebnisse über das Verhalten der Molybdatophosphorsäure über das vorliegende Problem hinaus von Bedeutung sind.

I. VERTEILUNG VON MOLYBDATOPHOSPHORSÄURE ZWISCHEN DEN LÖSUNGSMITTELN WASSER UND ÄTHYLACETAT

STOLL[3] benutzte erstmalig dieses Verfahren[4], und zwar zur Bestimmung des geringen Phosphorsäuregehaltes im Meerwasser. WURZSCHMITT UND SCHUHKNECHT[5] wandten es zur Trennung der Ortho- von Pyro- und Metaphosphorsäure an. In beiden Untersuchungen werden für die Bedingungen, unter denen die Extraktion vorgenommen werden soll, enge Grenzen angegeben. Wir interessierten uns dafür, wie weit man auch bei Überschreitung dieser Werte noch vollständige Extraktion erzielt, und prüften deshalb die Verteilung der Phosphorsäure und des Molybdäns(VI) einzeln und gemeinsam unter Variation der Konzentrationen an den Komponenten und an freier Säure (Salz-bezw. Schwefelsäure). Anschliessend wurde der Einfluß von V und Fe untersucht.

Zur *Ausführung der Versuche* wurden in einem Schüttelzylinder abgemessene Volumina von Lösungen bekannten Gehaltes von Na_2HPO_4, Na_2MoO_4 und Salz- bezw. Schwefelsäure gemischt und — evtl. nach Auflösen einer gewogenen Menge NaCl — auf 125 ml mit Wasser aufgefüllt. Ammoniumsalze durften nicht verwandt werden, weil sonst die Fällung von Ammoniummolybdatophosphat gestört hätte. Die angewendeten Mengen der Salze sind in den Spalten 2-4 der Tab. I

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* 12. Mitteilg. über die Trennung anorganischer Stoffgemische durch Verteilen. 11. Mitteilg.: W. FISCHER *et al.*, Über die Trennung der Seltenen Erden durch Verteilen. *Angew. Chem.*, 66 (1954)317.

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TABELLE I

VERTEILUNG VON PHOSPHOR(V) UND MOLYBDÄN(VI) ZWISCHEN SAURER WÄSSRIGER LÖSUNG UND ÄTHYLACETAT

Vers. Nr.	*wässr. Phase vor der Verteilung*			*überschüss. Säure val/l*	*Prozentische Extraktion*		*mg P_2O_5 in der gesamten Esterphase*	*Atomverhältnis P : Mo im Ester*
	mg P_2O_5 als Na_2HPO_4	*g Mo als Na_2MoO_4*	*g NaCl*		P_P	P_{Mo}		
		in 125 ml						
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
				HCl				
1	42.5	—	—	0.19	0.2	—	—	—
2	42.5	—	10	0.19	<0.2	—	—	—
3	42.5	—	—	6.0	∼1	—	—	—
4	—	1.6	—	—0.02*)	—	0.03	—	—
5	—	1.6	9.4	—0.02*)	—	0.02	—	—
6	—	2.5	—	0.06	—	0.02	—	—
7	—	2.5	10	0.06	—	0.03	—	—
8	—	1.6	—	1.2	—	0.5	—	—
9	—	1.6	—	2.1	—	11	—	—
10	—	1.6	—	5.8	—	90	—	—
11	—	0.25	—	6.0	—	91	—	—
12	42.5	3.0	—	—0.26**	<0.3	—	—	—
13	42.5	3.0	—	—0.02*)	96.7	—	—	—
14	42.5	1.6	—	—0.02*)	86	38	—	1:11.9
15	42.5	1.6	9.4	—0.02*)	99.8	—	—	—
16	0.092	1.6	9.4	—0.02*)	—	—	0.088	—
17	42.5	1.6	—	0.14	99.7	48	—	1:11.95
18	0.085	1.6	—	0.14	—	—	0.081	—
19	0.085	1.6	9.4	0.14	—	—	0.087	—
20	42.5	1.6	—	0.54	99.6	46	—	—
21	0.085	1.6	—	0.54	—	—	0.088	—
22	42.5	1.6	—	0.94	99.8	48	—	1:12.4
23	42.5	1.6	—	1.2	99.7	47	—	1:12.2
24	42.5	1.6	—	1.5	99.7	—	—	—
25	42.5	1.6	—	2.1	96	—	—	—
26	42.5	1.6	—	5.9	7	87	—	1:1170
				H_2SO_4				
27	42.5	1.6	—	0.14	89	—	—	—
28	42.5	1.6	9.4	0.14	99.9	—	—	—
29	0.085	1.6	—	0.14	—	—	0.081	—
30	0.085	1.6	9.4	0.14	—	—	0.084	—
31	42.5	1.6	—	0.54	99.7	—	—	—
32	0.085	1.6	—	0.54	—	—	0.083	—
33	42.5	1.6	—	0.94	99.8	—	—	—
				HCl				
34	42.5	0.25	—	0.08	—	92	—	—
35	212.5	0.25	—	0.16	—	95	—	—
36	42.5	0.25	—	0.21	41	99.9	—	1:11.9
37	42.5	0.25	—	0.36	—	95	—	—
38	42.5	0.25	—	2.4	0.4	29	—	1:675
39	42.5	0.25	—	6.0	3	92	—	1:392

* pH = ∼ 2

** pH = 5-6

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aufgeführt. Die in Spalte 5 angegebene Konzentration an „überschüssiger Säure" bedeutet die — in val/l ausgedrückte — Differenz, die sich durch Subtraktion der angewendeten Molybdat- und Phosphatmenge von der zugefügten Säuremenge nach Division durch das Volumen ergibt. Positive Werte dieser Grösse stellen ein ungefähres Maß für die Konzentration an freier Säure in der Mischung dar. In wenigen Fällen wurde ein geringer Unterschuss an Säure gegenüber den beiden Salzen angewendet; dann erscheinen in Spalte 5 negative Werte.

Nach Zugabe von 125 ml Äthylacetat wurde der Zylinder mit den beiden Phasen 4-mal je 15 sec geschüttelt und zwischendrein in ein Wasserbad von 20 ± 0.5° C gestellt, und zwar die ersten beiden Male etwa je 15 min, nach dem 3. und 4. Schütteln kürzere Zeit. Bei den Versuchen mit $6N$ Säurekonzentration schüttelte man nur 3-mal und kürzte die Temperierungszeiten ab, um das Ausmaß der Verseifung des Esters möglichst gering zu halten. Anschliessend wurden die Volumina der beiden Phasen an der Kalibrierung, mit der der Schüttelzylinder versehen war, abgelesen. Bei der Mehrzahl der Versuche nahm das Volumen der Esterphase um 5-10 ml ab, das der Wasserphase um fast den gleichen Betrag zu; nur bei den Versuchen mit $6N$ Salzsäure waren die Änderungen grösser (bis 40 ml).

Soweit nichts anderes angegeben, wurden einige Minuten nach dem letzten Schütteln Anteile beider Phasen *zur Analyse* entnommen. Bei extremer Verteilung zugunsten einer der beiden Phasen filtrierte man diejenige mit der geringeren Konzentration zur Befreiung von emulgierten Tröpfchen der anderen durch ein trockenes Filter. In diesen Fällen wurde meist nur die verdünntere Phase analysiert und der Gehalt der anderen als Differenz gegen die Einwaage errechnet. Zur Analyse wurden je nach den vorliegenden Partnern und den Mengenverhältnissen verschiedene Verfahren benutzt, die sämtlich zuvor an gleichartigen Mischungen bekannten Gehaltes erprobt worden waren.

Zur *Phosphorbestimmung* ist folgendes zu bemerken: P_2O_5-Mengen von 1-45 mg wurden nach VON LORENZ[6] als Ammoniummolybdatophosphat gefällt und ausgewogen und mit dem empirischen Faktor 0.03295 auf P_2O_5 umgerechnet. Zur Vermeidung einer Ausscheidung von Molybdänsäure erwies es sich als zweckmässig, nicht nach der Literaturvorschrift das kalte Fällungsreagens in die 95° C warme Lösung zu giessen, sondern beide zuvor auf 60° C zu erwärmen. Nach diesem Verfahren erhielten wir bei grösseren P_2O_5-Mengen auch gute Werte bei Anwesenheit von Vanadin(V) in Mengen bis zu 20 mg; anscheinend wird die bei anderen Ausführungsformen der Molybdatophosphatfällung meist beobachtete Mitfällung von Vanadin(V) hier durch die relativ hohe HNO_3- und Molybdat-Konzentration stark vermindert. — P_2O_5-Mengen von 0.1-1 mg wurden analog im Mikromaßstab bestimmt.

Kleinere P_2O_5-Mengen von etwa 5 μg aufwärts wurden bei Abwesenheit von V und Fe als Molybdänblau photometrisch bestimmt. War eine wässrige Lösung zu untersuchen, so wurde sie unter den von WURZSCHMITT UND SCHUHKNECHT[5] angegebenen Bedingungen mit Äthylacetat extrahiert; das war zulässig, nachdem sich (z.B. durch den Versuch Nr. 16 der Tab. I) ergeben hatte, daß so auch kleine P_2O_5-Mengen vollständig extrahiert werden. Nach Filtration durch ein trockenes Filter unter Verwerfen der ersten Anteile wird ein Teil des Esters in eine Küvette gebracht und in Anlehnung an STOLL[3] darin mit 1 Tropfen $SnCl_2$-Lösung (1.2 g $SnCl_2 \cdot 2\,H_2O$ + 20 ml konz. Salzsäure + 80 ml H_2O) reduziert; dabei wird mit einem Glasstab vorsichtig umgerührt, ohne die Wände zu berühren. Ist die Lösung trübe, so fügt man einen oder wenige Tropfen Äthylacetat zu; das ist zulässig, wenn die Volumenänderung klein gegenüber der Fehlergrenze des Verfahrens bleibt (nach unseren Erfahrungen ± 5 bis höchstens ± 10%). Wir haben diese Lösung dann gegen reines Äthylacetat im Pulfrich-Photometer mit dem Filter L 1 (max. Durchlässigkeit bei 680 mμ) gemessen. — Lag die zu bestimmende Phosphorsäuremenge bereits als Molybdatophosphorsäure im Ester vor, so konnte sie unmittelbar mit $SnCl_2$ reduziert und photometriert werden. — Bei dem beschriebenen Verfahren stören im Gegensatz zu den Molybdänblaumethoden ohne Extraktion weder Kiesel- noch Arsensäure, weil diese nicht mit extrahiert werden[3,4,5].

Zur *Auswertung* wurde aus den analytisch ermittelten Konzentrationen in der Esterphase c_e und in der Wasserphase c_w die prozentische Extraktion $P = \frac{c_e \cdot 100}{c_e + c_w}$ ermittelt und in Tab. I, Spalte 6 und 7, angegeben. Diese Grösse stellt den prozentischen Anteil der angewandten Menge des betreffenden Elementes dar, der durch die Esterphase extrahiert wird unter der Voraussetzung, daß die Volumina der beiden Phasen *nach* Einstellung des Verteilungsgleichgewichtes gleich gross sind. Der Extraktionskoeffizient $\alpha = c_e/c_w$ lässt sich daraus durch die Beziehung $\alpha = P/(100\text{-}P)$ ermitteln. — Bei weitgehender Extraktion sehr kleiner Mengen Phosphorsäure verblieb eine so geringe Konzentration c_w in der Wasserschicht, daß diese analytisch nicht mehr fassbar war. In

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diesen Fällen errechneten wir aus der Konzentration der Esterphase und ihrem Volumen die Menge P_2O_5 in der gesamten Esterphase (Spalte 8). Durch Vergleich mit der angewandten Menge P_2O_5 (Spalte 2) lässt sich die Vollständigkeit der Extraktion beurteilen.

Die *Ergebnisse* sind in Tab. I zusammengestellt. Etwa die Hälfte der Zahlen stellt Mittelwerte von Parallelversuchen dar. Die dabei erhaltenen P-Werte stimmten bei sehr geringer und sehr weitgehender Extraktion meist auf ± 0.1% überein; nur bei hoher Säurekonzentration war die Reproduzierbarkeit manchmal schlechter, wohl als Folge teilweiser Verseifung des Esters. Bei mittlerer Extraktion waren die Schwankungen stets grösser (∼ 2-3%), weil hier die prozentische Extraktion bei geringen Änderungen der Ausgangsbedingungen (z.B. H^+-Konzentration) stark variiert.

Phosphorsäure allein wird nur in geringem Masse extrahiert (Versuche Nr. 1-3). Natriumchlorid, das wir in Anlehnung an die Arbeitsvorschrift von WURZSCHMITT UND SCHUHKNECHT[5] bei einem Teil der Versuche in hoher Konzentration zufügten, scheint die Extrahierbarkeit der Phosphorsäure bei Abwesenheit von Molybdat wenig zu beeinflussen (Nr. 2). — *Molybdän(VI) allein* wird mit steigender Säurekonzentration zunehmend stärker extrahiert (Nr. 4-11); dabei dürfte — wie bei der Extraktion mit Äther[7] — die Verbindung $MoO_3 \cdot 2\ HCl$ bezw. $H_2[MoO_3Cl_2]$ in das organische Lösungsmittel übergehen.

Bei den Versuchen Nr. 12—26 wurde *Phosphorsaüre mit einem Überschuss von Molybdat* angewendet. Einem Atomverhältnis 1 P : 12 Mo würde ein Gewichtsverhältnis von 42.5 mg P_2O_5 : 690 mg Mo entsprechen. Die prozentische Extraktion der Phosphorsäure steigt zunächst mit dem Säuregehalt der wässrigen Lösung bis auf 99.8% an. Bei unvollständiger sowohl wie bei praktisch vollständiger Extraktion der Phosphorsäure werden bei Konzentrationen des Säureüberschusses bis 1.2*N* auf 1 Atom P ziemlich genau 12 Atome Mo mit extrahiert (Spalte 9). Hier geht also die Dodekamolybdatophosphorsäure (oder ihre Salze; vgl. unten) in den Ester über. Bei Säurekonzentrationen >2*N* sinkt die Extraktion des Phosphors, während die des Molybdäns zunimmt, so daß das Verhältnis P : Mo im Ester extreme Werte erreicht. Diese Befunde stehen in Einklang mit den Beobachtungen von JANDER[8]. Darnach bildet sich die Dodekamolybdatophosphorsäure in wässriger Lösung erst unterhalb etwa pH = 1, während sie sich unterhalb pH = 0 wieder zu zersetzen beginnt und dann bei steigender Wasserstoffionenkonzentration mit steigenden Konzentrationen von Molybdänylkationen im Gleichgewicht steht. Mit Äthylacetat extrahierbar sind augenscheinlich nur die Dodekamolybdatophosphorsäure und die — phosphorfreien — Molybdänylverbindungen.

Wie die Versuche Nr. 13 und 15 im Vergleich zu Nr. 14 zeigen, steigern einerseits erhöhte Molybdatkonzentration und andererseits NaCl-Zusatz den Umfang der Extraktion der Molybdatophosphorsäure unter den vorliegenden Bedingungen. — Kleine Phosphorsäuremengen (Versuche Nr. 16, 18, 19, 21) werden nach Extraktion im günstigen Bereich der Säurekonzentration in der Esterphase innerhalb der Fehlergrenze vollständig wiedergefunden.

Bei der Verwendung von *Schwefelsäure* anstelle von Salzsäure beginnt der Bereich, in dem man ohne NaCl-Zusatz praktisch vollständige Extraktion erzielt, erst bei etwas höherem Säureüberschuß (Nr. 27-33).

Interessant war die Frage, wie die Extraktion bei Verwendung eines *Unterschusses an Molybdat* erfolgt (Nr. 34-39). Es zeigte sich, daß bei einem Gewichtsverhältnis von 42.5 P_2O_5 : 250 Mo entsprechend einem Atomverhältnis von 1 P : 4.35 Mo nunmehr das *Molybdän* fast vollständig extrahiert werden kann, aber nur in einem engen Bereich des Säureüberschusses (vgl. Nr. 34-37). Dabei geht wiederum auf 12 Atome Mo 1 Atom P in den Ester über. Bei hoher Säurekonzentration (Nr. 38, 39) treten grundsätzlich dieselben Erscheinungen auf wie bei Molybdatüberschuss (Nr. 25, 26).

In einer Reihe von Versuchen wurde ferner geprüft, ob auch *Natrium* mit in die Esterphase übergeht. Unter den Bedingungen der Versuche Nr. 14 bezw. 17 der Tab. I fanden wir im Ester das Atomverhältnis Na : P : Mo = 2.1 : 1 : 11.9 bezw. 0.7 : 1 : 11.9_5. Es werden also saure Natriumsalze der Heteropolysäure extrahiert, und zwar aus der stärker sauren Ausgangslösung relativ weniger Natrium. Daß die Extraktion des Natriums tatsächlich an diejenige des P-Mo-Komplexes geknüpft ist, ergibt sich daraus, daß bei einem weiteren Versuch analog Nr. 14, aber *ohne* Zusatz von Phosphat, die Natriummenge im Ester 100-mal geringer war als bei Anwesenheit von Phosphat.

Zeiteffekte: Bei einem Teil der Versuche (z.B. Nr. 14, 15, 22) wurde die wässrige Lösung vor der Extraktion bis zu 15 Std. bei Raumtemperatur stehen gelassen. Die Ergebnisse deckten sich mit denen von möglichst rasch durchgeführten Parallelversuchen. Die Bildungsgeschwindigkeit der Heteropolysäure ist also so gross, daß sie auf unsere Versuche ohne Einfluß ist. Dafür spricht auch eine Beobachtung bei den Versuchen Nr. 23 und 24. Die wässrige Phase war vor dem Ausschütteln nicht so tief gelb gefärbt wie entsprechende Lösungen geringerer Säurekonzentration, zweifellos deshalb, weil sich die Molybdatophosphorsäure bei einer Konzentration des HCl-Überschusses von 1.2-1.5*N* während der Zeit, die bis zur Extraktion verstrich, nicht mehr vollständig bildet. Trotzdem wurde sie praktisch vollständig extrahiert. Das widerspricht nicht der Feststellung von JANDER UND WITZMANN[8], daß sich das Gleichgewicht in wässrigen Lösungen bei Säurekonzentrationen über 1*N* erst nach einigen Wochen einstellt. Denn in unserem Falle wird durch die Extraktion die Molybdatophosphorsäure laufend aus der wässrigen Lösung entfernt, so daß sie in dieser Phase augenscheinlich genügend rasch nachgebildet werden kann bis zum praktisch vollständigen Umsatz der Phosphorsäure. — Ließ man die beiden Phasen von Versuchen mit 42.5 mg P_2O_5 einige Stunden lang stehen, ohne sie zu trennen, so färbte sich die Wasserphase unterhalb der Grenzfläche langsam blau. Anscheinend reduziert der durch Verseifung des Esters entstehende Alkohol Molybdatophosphorsäure.

Einfluß von Vanadin: Bei den folgenden Versuchen wurden je 440 mg V als $NaVO_3$ oder $VOSO_4$ neben 42.5 mg P_2O_5 als Na_2HPO_4 oder 1.6 g Mo als Na_2MoO_4 oder neben diesen Mengen beider Stoffe in 125 ml wässriger Lösung angewendet und mit 125 ml Äthylacetat extrahiert. Zur Einstellung der Säure konzentration dienten HCl und H_2SO_4. Phosphor und Molybdän werden, wenn nur eines dieser Elemente mit 5- oder 4-wertigem Vanadin gemischt wird, aus einer Lösung mit 0.5*N* Konzentration des Säureüberschusses ebenso wenig extrahiert wie bei Abwesenheit von Vanadin; dieses selbst geht nur in der Kombination mit Mo zu einigen 1/10 mg in 125 ml Ester über. Bei gleichzeitiger Gegenwart von 5-wertigem V, P und Mo werden einige mg V, aber nur geringe, von Versuch zu Versuch wechselnde Anteile der Phosphorsäure ($\sim$15%) extrahiert. 5-wertiges Vanadin stört also unter diesen Bedingungen stark. 4-wertiges V hingegen gestattet eine 99.5%ige Extraktion der Molybdatophosphorsäure, dabei liegt aber die mindestens erforderliche Konzentration an überschüssiger Säure bei etwas höheren Werten als in Abwesenheit von V. Das rührt daher, daß augenscheinlich das V^{IV} bei geringer H^+-Ionen-Konzentration das Molybdatophosphat langsam zu Molybdänblau reduziert. Das machte sich durch Farbänderung der Lösungen und dadurch bemerkbar, daß aus schwächer sauren Lösungen umso weniger Molybdatophosphorsäure extrahiert wurde, je länger sie vor der Extraktion gestanden hatten. Bei 0.9*N* Säureüberschuß-Konzentration gehen immerhin bei sofortiger Extraktion 99.5% der Molybdatophosphorsäure in den Ester über, in 1.2 bis 1.5*N* Säure tritt auch bei 1-stündiger Wartezeit keine Störung mehr auf. Bei diesen Bedingungen gehen von dem

Vanadin 2-4 mg mit in 125 ml Ester über, stören darin aber die Phosphorbestimmung nicht, wenn man sie nach VON LORENZ vornimmt (s. S. 3). Das Atomverhältnis P : Mo im Ester ist auch hier stets nahe 1 : 12.

Einfluß von Eisen: Eisen (II) reduziert unter den für die Extraktion günstigen Bedingungen die Molybdatophosphorsäure momentan zu Molybdänblau. Die folgenden Versuche wurden mit je 600 mg Eisen(III) als $FeCl_3$ — evtl. neben den im vorstehenden Absatz angegebenen Mengen der anderen Partner — in salz- und schwefelsauren Lösung ausgeführt. Von dieser Eisenmenge gehen aus einer 1.2*N* säuren Lösung 3 mg Fe in 125 ml Ester über, wenn man es allein anwendet; durch Zusatz der Partner P, Mo, V^{IV} einzeln oder gemeinsam wird diese Zahl wenig geändert (2-5 mg Fe). Bei 1.2-1.5*N* Säureüberschuß und Anwesenheit von Fe und Mo oder Fe, Mo und V^{IV} wird Phosphorsäure stets zu über 99% extrahiert. Eine 1-stündige Wartezeit vor dem Ausschütteln ist ohne Einfluß.

In 4 Versuchen wurden schliesslich kleine bekannte Phosphorsäuremengen mit 1.6 g Mo^{II} und je 400-600 mg V^{IV} und Fe^{III} auf 125 ml wässriger Lösung, deren Konzentration an überschüssiger Säure (Salz- und Schwefelsäure) 1.2*N* oder 1.5*N* war, gebracht und mit 125 ml Ester extrahiert. 100 ml Ester wurden zur Trockne gedampft; den Rückstand rauchte man mit wenig konz. HNO_3 ab, weil er beim Abdampfen des Esters zum Teil reduziert worden war, versetzte ihn mit NH_3-Lösung und dann mit HNO_3 und fällte nach VON LORENZ (s. S. 2). Auf das Gesamtvolumen des Esters umgerechnet, wurden 0.281 bezw. 0.272 mg P_2O_5 (gegeben: 0.261) und 2.86 bezw. 2.80 mg P_2O_5 (gegeben: 2.96) gefunden.

II. TRENNUNG DURCH KATIONENAUSTAUSCH

Orthophosphorsäure lässt sich nach SALMON UND TIETZE[9] von Vanadin(IV), nach KORTÜM U. MITARB.[10] und SAMUELSON[11] von Eisen(III) durch Kationenaustauscher trennen, wenn die beiden Partner in Mengen gleicher Grössenordnung vorliegen oder die Phosphorsäure überwiegt. Dagegen stellten wir in Übereinstimmung mit ähnlichen Versuchen von KORTÜM und Mitarb.[10] fest, daß z.B. aus einer ∼ 0.2*N* schwefelsauren Lösung bei einem Gewichtsverhältnis von $Fe^{III} : P = 300 : 1$ fast die Hälfte der Phosphorsäure von dem Kationenaustauscher festgehalten wird. Dafür sind, wie schon KORTÜM annahm, sicherlich kationische Eisen-Phosphorsäurekomplexe verantwortlich. Die Störung läßt sich am einfachsten dadurch beheben, daß man das Eisen vor dem Ionenaustausch mit SO_2 zur 2-wertigen Stufe reduziert; dabei wird zugleich das Vanadin zu VO^{+2} reduziert, das sich, wie wir fanden, auch in grossem Überschuß störungsfrei durch den Austauscher von der Phosphorsäure trennen lässt.

Als *Kationenaustauscher* verwendeten wir Lewatit KS 22 von den *Bayer*-Werken, ein Präparat auf Phenol-Formaldehyd-Basis mit Sulfosäuregruppen, in der Körnung von 0.1 bis 0.3 mm. 80 g des lufttrockenen Materials (Kapazität: 2.3 mval/g) wurden in die H^+-Form überführt und unter den üblichen Vorsichtsmaßregeln in eine Säule von 2 cm Ø und 40 cm Länge gefüllt. Da es schwierig ist, den Austauscher durch Behandlung mit Salzsäure völlig von Eisen zu befreien, ist es erforderlich, ihn vor der Verwendung zu dem vorliegenden Zweck in der Säule einmal mit wässriger schwefliger Säure zu spülen, bis das Filtrat darnach riecht. Andernfalls wurden beim Durchsetzen von Phosphorsäure (∼ 1 mg P) 5% derselben von der Säule festgehalten. Bei mehrfacher Benutzung der gleichen Säule erwies sich nach ihrer Regeneration mit Salzsäure eine erneute Behandlung mit schwefliger Säure nicht als notwendig.

Arbeitsweise: Die Analysenlösung (Volumen: 75-100 ml) und das anfänglich in kleinen Anteilen aufgegebene Waschwasser ließ man mit einer Geschwindigkeit von ∼ 15 ml/min durchfliessen. Es wurden stets 250 ml Filtrat aufgefangen, nachdem man sich überzeugt hatte, daß in weiteren 100 ml Filtrat nur noch $< 0.1\%$ der angewendeten, vom Austauscher nicht gebundenen Anionen enthalten waren.

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Zur *Prüfung der erzielbaren Trennschärfe* wurden Lösungen, die in 75-100 ml 300 mg Fe^{III} und 300 mg V^{V} neben 0.3-1 mg P^{V} enthielten und 0.1-0.2*N* an freier Schwefelsäure waren, zunächst reduziert, indem man sie zum Sieden erhitzte, von der Flamme nahm und dann solange einen kräftigen SO_2-Strom einleitete, bis etwa ausgeschiedene Vanadinsäure wieder gelöst und die Farbe der Lösung rein blau geworden war. Diese Operation erforderte etwa 10-15 min. Nach dem Abkühlen der Lösung auf mindestens 30-40° C wurde sie auf die Säule aufgegeben. Im Filtrat liess sich mit H_2O_2 kein V und — nach Oxydation — mit NH_4SCN kein Fe mehr nachweisen. In 14 Versuchen, die z.T. unter etwas variierten Bedingungen durchgeführt wurden, fand man angewendete Phosphormengen von etwa 0.3 bezw. 1 mg mit einer max. Abweichung von ± 8 bezw. ± 2% vollständig im Filtrat.

Eine Verlängerung der Dauer des SO_2-Einleitens sowie dauernde Erhitzung währenddessen änderte die Ergebnisse nicht. Dasselbe gilt, wenn die Reduktion mit mehreren kleinen Portionen von festem Natriumsulfit vorgenommen wird; nur muss dabei auf dauernde Anwesenheit freier Schwefelsäure geachtet werden. Auch war kein Einfluß auf das Resultat zu beobachten, wenn man die überschüssige schweflige Säure vor dem Ionenaustausch fortkochte; doch wird man dies zweckmässiger erst danach vornehmen.

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ZUSAMMENFASSUNG

Die Extraktion von Phosphorsäure als Molybdatokomplex aus wässriger, saurer Lösung mittels Äthylacetat wird in Abhängigkeit von den Konzentrationen der Partner und der Wasserstoffionen sowie bei Gegenwart grosser Überschüsse an Fe und V untersucht. Die Abtrennung dieser beiden Elemente gelingt innerhalb eines bestimmten Konzentrationsbereiches an freier Säure weitgehend. Die Phosphorsäure geht in Form saurer Natriumsalze der Dodekamolybdatophosphorsäure in die Esterphase über. Die Konzentrationseinflüsse der Partner und der H+-Ionen werden gedeutet. — Kleine Phosphorsäuremengen lassen sich durch Kationenaustauscher (Lewatit KS *22*) nicht von viel Eisen(III), sehr gut aber von Eisen(II) und Vanadin(IV) trennen.

SUMMARY

The extraction of phosphoric acid as the molybdate complex from aqueous acid solution by means of ethyl acetate has been examined, with regard to the concentration of the two constituents and the hydrogen ion concentration and in the presence of a large excess of Fe and V. The separation of these two elements can be achieved within a certain range of concentration in free acid. The phosphoric acid is obtained in the form of acid sodium salts of dodecamolybdic acid in the esterphase. The influence of the concentration of the constituents and the hydrogen ion concentration is pointed out. Using a cation exchanger (Lewatit KS *22*) small quantities of phosphoric acid can not be separated from large amounts of iron(III), but the separation from iron(II) and vanadium(IV) is very successful.

RÉSUMÉ

L'extraction de l'acide phosphorique comme molybdatocomplexe, au moyen de l'acétate d'éthyle été examinée en fonction de la concentration des deux constituants et de la concentration des ions hydrogène, et en présence de gros excès de fer et vanadium. La séparation de ces deux éléments peut s'effectuer dans une certaine limite de concentration en acide libre. Dans la phase organique l'acide phosphorique prend la forme du sel acide de sodium de l'acide dodécamolybdatophosphorique. L'influence des concentrations des constituants et des ions hydrogène est interprétée. De petites quantités d'acide phosphorique ne peuvent pas être séparées de grandes quantités de fer(III) par un échangeur de cations (Lewatit KS *22*); par contre la séparation d'avec le fer(II) et le vanadium(IV) est très bonne.

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DE L'EXTRACTION DES COLORANTS POUR DENRÉES ALIMENTAIRES AVEC LA QUINOLÉINE ET DE LEUR IDENTIFICATION PAR CHROMATOGRAPHIE SUR PLAQUE D'ALUMINE

par

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INTRODUCTION

Cette communication représente — sous forme condensée — l'aboutissement de longs travaux effectués dans notre Laboratoire sur la recherche et l'identification des colorants artificiels dans les denrées alimentaires, travaux qui ont déjà fait l'objet de quatre publications[1 à 4]. On sait, en effet, qu'il est d'usage dans la plupart des pays de colorer artificiellement certains aliments pour en améliorer l'aspect. Les diverses législations en la matière en tiennent compte et autorisent l'emploi d'un certain nombre de colorants duement stipulés qui varient quelque peu d'un pays à l'autre[5].

La recherche d'une coloration artificielle présente donc un grand intérêt, tant pour déceler cette dernière dans un aliment où elle est défendue que pour découvrir si c'est bien un colorant autorisé qui a été utilisé là où elle est permise. Cette recherche est d'autant plus importante que certains colorants non autorisés ne sont pas inoffensifs; elle consiste en:

I. l'isolement du colorant et
II. son identification.

I. *L'isolement du colorant* est rendu nécessaire par:

1. la faible quantité qui en est généralement utilisée du fait du fort pouvoir colorant de ces substances, et
2. le mode d'identification choisi, c'est-à-dire la chromatographie, qui exige d'avoir aussi peu que possible de substances étrangères présentes.

Cet isolement revient à enrichir et à purifier le colorant; on l'effectuait généralement par des teintures sur laine et sur coton[6 à 10]. On a aussi proposé d'extraire les colorants avec divers dissolvants organiques comme, par exemple, la méthylcyclohexanone[11], l'alcool benzylique[12], l'éther[6] et, surtout, l'alcool *iso*amylique[7, 13 à 24]. Ces deux méthodes présentent toutefois les inconvénients suivants:

a) Les essais de teinture, qu'on fait à chaud, ainsi que le démontage ultérieur du colorant en milieu ammoniacal, ne sont pas sans exercer une certaine influence sur des

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colorants sensibles. On le constate facilement en chromatographiant une solution de colorant pur et la solution du même colorant isolé dans un essai de teinture.

b) Les dissolvants cités n'extraient *pas tous* les colorants autorisés; de plus, on est obligé — pour obtenir une extraction quantitative — de travailler à divers pH, par exemple d'abord en milieu neutre ou faiblement acide puis en milieu fortement acide. Or, certains colorants sont sensibles aux acides forts, ce qui fait que ce mode opératoire n'est pas toujours recommandable[25 et 25 bis].

On s'est donc proposé de rechercher et de mettre au point une méthode d'extraction des colorants qui exclue, autant que possible, tout traitement thermique ainsi que tout réactif énergique et qui soit, de plus, simple, pratique et rapide. On y est parvenu, pour (1) *les colorants liposolubles*, en dissolvant la matière grasse colorée dans un dissolvant de très faible pouvoir éluant et en adsorbant le colorant sur alumine. Un colorant en substance peut être examiné soit directement, après dissolution dans un dissolvant approprié, par ex. le benzène (technique de la goutte, *cf.* partie expérimentale), soit après adsorption sur alumine (technique de la poudre, *cf.* partie expérimentale); (2) *les colorants hydrosolubles*, en préparant une solution ou une suspension aqueuse de l'aliment coloré, en l'extrayant avec la quinoléine et en isolant le colorant de la quinoléine.

Un colorant en substance peut être examiné soit directement, en solution, soit après adsorption sur alumine (voir ci-dessus). On a trouvé que la quinoléine * est nettement supérieure aux dissolvants proposés jusqu'à présent et, notamment, à celui le plus fréquemment recommandé: l'alcool *iso*amylique. En effet, elle a extrait *complètement* les 43 colorants examinés, comprenant notamment tous ceux autorisés en Suisse (pour la tartrazine seulement, l'extraction a dû être répétée une ou deux fois pour être complète).

II. *L'identification des colorants* est faite par *chromatographie sur plaque d'alumine, par comparaison avec les colorants autorisés traités de la même façon* et en recourant éventuellement à d'autres examens (réactions à la touche, fluorescence en lumière ultraviolette, *etc.*). Cette méthode d'identification permet un travail rapide (20-30 minutes en général) avec de faibles quantités de colorants (jusqu'à quelques gammas); de plus, plusieurs chromatogrammes peuvent être faits sur la même plaque, ce qui est important pour les comparaisons car la mesure du facteur R_F ne saurait suffire seule à une identification certaine. En effet, comme divers facteurs influent sur le R_F d'unes ubstance il s'ensuit que des variations de ce dernier sont possibles. Ces variations sont évitées en ayant le colorant à identifier placé à côté des colorants de référence, sur la même plaque. On réunit ainsi les avantages de la chromatographie sur alumine (fort pouvoir séparateur, *etc.*) avec ceux de la chromatographie sur papier (travail avec de petites quantités de substance, comparaisons, *etc.*). On a constaté qu'on peut effectuer ainsi facilement des séparations impossibles ou très difficiles à réaliser sur papier. D'autre part, la technique du report d'une tache sur une autre plaque, décrite dans ce travail (*cf.* partie expérimentale), équivaut à faire une chromatographie à deux dimensions, qui peut même être poussée plus loin en reportant les taches, après développement, sur d'autres plaques encore.

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* RUGGLI ET JENSEN[26] ont chromatographié un colorant en solution quinoléique, mais il ne semble pas que la quinoléine ait été utilisée jusqu'à présent pour l'extraction des colorants.

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PARTIE EXPÉRIMENTALE

I. ISOLEMENT DES COLORANTS

L'isolement des colorants diffère suivant que ceux-ci sont liposolubles ou hydrosolubles.

1. Colorants liposolubles

a) Réactifs :

Pentane, P.E. 32-34° C (éventuellement éther de pétrole de bas P.E.).

Alumine, qualité standardisée selon BROCKMANN, hautement activée par chauffage de 3/4 d'heure à 1 heure à 300-500° C et conservée en flacon hermétiquement bouché[27].

b) Mode opératoire

Prendre environ 5 g * de graisse, la dissoudre dans 50 ml de pentane et ajouter à la solution environ 0.5 g d'alumine. Bien agiter. Décanter la solution et répéter l'adsorption avec encore 0.5 g d'alumine (deux adsorptions suffisent généralement). Décanter. Laver les deux alumines deux à trois fois avec un peu de pentane, les laisser sécher à l'air, puis passer aussitôt à l'examen chromatographique, après les avoir réunies et mélangées. Dans le cas d'un mélange de colorants, on peut aussi chromatographier les deux alumines séparément, car la première sera plus riche en colorant(s) aisément adsorbé(s) et la seconde en colorant(s) moins facilement retenu(s) d'où résulte une séparation préliminaire grossière.

Dans ce travail on a généralement utilisé le mélange des deux alumines. Si la graisse est fortement colorée, on recommande d'en réduire la quantité et, inversément, de l'augmenter si sa coloration est faible, la quantité d'alumine restant la même dans les deux cas.

Si du diméthylaminoazobenzène (jaune de beurre) est présent, ce qu'on contrôle en acidulant une partie aliquote de la solution avec un peu d'acide chlorhydrique (elle vire au rouge en présence de ce colorant), il faut l'isoler en milieu acide, car son adsorption s'en trouve facilitée; il suffit, pour cela, de prendre une alumine acide ou d'ajouter à la solution quelques gouttes d'acide chlorhydrique concentré.

Toutes les opérations décrites ci-dessus sont très rapides et se font en quelques minutes.

Dans le cas d'une margarine, il faut la fondre, séparer la graisse de la couche aqueuse et la filtrer à chaud (par ex. à l'étuve) sur un filtre plissé, puis opérer comme ci-dessus.

L'alumine colorée obtenue contient les colorants artificiels ajoutés à la matière grasse; quant aux carotinoïdes (carotène, *etc.*), ils restent pour la plupart dans la solution.

Les colorants examinés ont été les suivants:
soudan I; soudan II; soudan III; soudan IV; soudan G; rouge soudan G; diméthylaminoazobenzène; annatto; curcuma.

2. Colorants hydrosolubles

a) Réactifs :

Quinoléine, pure, du commerce. Sa couleur légèrement jaune, n'est pas gênante; si, toutefois, elle devait être plus forte, il serait recommandable de purifier ce dissolvant par distillation sous pression réduite. Conserver à l'abri de la lumière, en flacon bien bouché.

Tampon de pH 3 : dissoudre 3.5 g d'acétate de sodium dans un peu d'eau, ajouter 50 ml d'acide acétique glacial et étendre à 1 litre avec de l'eau distillée.

Alumine, hautement activée (voir sous Colorants liposolubles).

b) Mode opératoire

Comme il varie un peu selon les aliments, on le trouvera résumé dans le Tableau ci-après.

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* On a pu travailler fréquemment avec 1 g de graisse dans 25 ml de pentane, et 2 fois 0.1 g d'alumine

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Tableau pour l' anal

1. Préparation de la soluti

1.1. Matières colorantes en substance		1.2. Denrées alimentaires ne requérant aucune extraction		
1.1.1. Solubles dans l'eau	**1.1.2. Solubles dans l'alcool**	**1.2.1. Denrées liquides de moins de 15% d'éthanol**	**1.2.2. Denrées liquides de plus de 15% d'éthanol**	**1.2.3. Denrées solides ou s solubles dans l'eau**
Tous les colorants examinés sauf un.	1 seul parmi les colorants examinés: le bleu d'aniline soluble dans l'alcool.	— Boissons sans alcool; limonades; jus de fruits concentrés, avec et sans pulpe. — Moûts; cidres; vins; vins doux (de moins de 15% d'alcool). — Bière; vinaigre. — Arômes pour potages; etc.	— Vins doux. — Spiritueux. — Liqueurs.	— Gelées; miel; sucreries. — Extraits de viande. — Extraits de café.
Traitement Faire une solution concentrée.	*Traitement* Dissoudre dans de l'éthanol à 96%; étendre si nécessaire avec de l'eau distillée.	*Traitement* — Aucun. — Eventuellement dilution avec de l'eau distillée.	*Traitement* — Ramener la teneur en éthanol à moins de 15% par dilution avec de l'eau distillée, avec ou sans évaporation préalable, selon la teneur en alcool et celle en colorant.	*Traitement* — Dissoudre dans de l'eau — Eventuellement filtrer
		Remarques 1.2.1.1 Chasser le CO_2 en chauffant légèrement à 30° et en agitant vigoureusement. 1.2.1.2 S'il se forme une émulsion stable à l'extraction, recommencer sur une nouvelle portion diluée et déféquée avec la quantité minimum de réactif de *Carrez* (exemple: bière brune). 1.2.1.3 Les produits dont le pH est inférieur à 3 doivent être neutralisés (exemple: essence de vinaigre).		
Solution aqueuse	**Solution alcoolique**	**Solution aqueuse**	**Solution aqueuse**	**Solution aqueus**

2. Extraction

3. Extrac

3.1 Phase aqueuse

4. Chromato

(cf. 1) et 3))

nalyse des colorants

ution aqueuse à extraire

<table>
<tr><th colspan="2">ion préliminaire</th><th colspan="2">1.3. Denrées alimentaires requérant une extraction préliminaire</th></tr>
<tr><td>ou semi-solides,
au</td><td>1.2.4. Produits laitiers et denrées donnant des suspensions dans l'eau</td><td>1.3.1. Denrées ne contenant que peu ou pas de graisse</td><td>1.3.2. Denrées plus riches en graisse</td></tr>
<tr><td>ies.</td><td>— Lait; yoghourts; glaces; crème glacée.
— Poudres pour poudings; poudres pour crèmes; etc.</td><td>— Céréales; légumineuses; produits de boulangerie et de pâtisserie.
— Soupes; pâtes alimentaires.
— Confitures; conserves de fruits.</td><td>— Chocolats.
— Produits à base de viande, tels que saucisses; etc.</td></tr>
<tr><td rowspan="2">l'eau distillée.
rer ou centrifuger.</td><td rowspan="2"><i>Traitement</i>
— Les produits laitiers doivent être éventuellement légèrement dilués avec de l'eau distillée.
— Les poudres pour crèmes et poudings doivent être mises en suspension avec beaucoup d'eau distillée.</td><td><i>Traitement</i>
— Broyer très finement la substance, éventuellement avec du sable.</td><td><i>Traitement</i>
— Broyer très finement la substance, éventuellement avec du sable.
— Epuiser avec de l'éther de pétrole ou du pentane (qui peut contenir, à part la graisse, des colorants liposolubles (cf. 1) et 3)).</td></tr>
<tr><td colspan="2">— Introduire 5 à 10 g de poudre ou de bouillie dans un erlenmeyer.
— Ajouter 30 à 40 ml d'éthanol à 70%.
— Laisser digérer quelques heures en agitant souvent.
— Décanter le liquide.
— Extraire avec une nouvelle portion d'éthanol à 70%.
— Réunir les extraits alcooliques et les ramener à moins de 15% d'alcool (voir sous 1.2.2).</td></tr>
<tr><td></td><td>Remarques
1.2.4.1 Les produits laitiers peuvent contenir des colorants liposolubles, qui sont partiellement extraits par la quinoléine. Ces colorants restent dans la couche éthérée (cf. sous 14) dont ils sont retirés avec l'alumine (cf. 1) et (3).
1.2.4.2 Le colorant étant souvent fixé sur la phase solide, il convient de ne pas séparer cette dernière de la phase liquide.</td><td colspan="2">Remarques
1.3.1.1 L'extraction à chaud au bain-marie est plus rapide, mais attention aux colorants sensibles à la chaleur.
1.3.1.2 Si l'extraction est difficile il faut ajouter quelques ml de quinoléine à l'alcool à 70%. Le traitement se fait comme ci-dessus.
1.3.1.3 En présence de laques etc., il convient d'ajouter un peu d'HCl concentré à l'alcool à 70%. Après l'extraction on neutralise prudemment et on continue comme sous 1.2.2.</td></tr>
<tr><td>queuse</td><td>Suspension aqueuse</td><td>Solution aqueuse</td><td>Solution aqueuse</td></tr>
</table>

on du colorant de la solution ou suspension aqueuse

— 1 partie de solution aqueuse + 1 partie de tampon pH 3 (= 10 à 200 ml au total).
— + 10 à 20 ml de quinoléine.
— Agiter, centrifuger, séparer, répérer si nécessaire.

Solution quinoléique

raction du colorant de la solution quinoléique

— 1 vol. de solution quinoléique + 3 vol. d'éther + 1 à 2 ml d'eau.
— Agiter, centrifuger, séparer.

3.2 **Phase organique**

Si celle-ci est encore colorée, lui ajouter un peu d'alumine hautement activée pour adsorber le colorant, agiter, centrifuger, décanter le liquide, laver l'alumine 2 ou 3 fois avec de l'éther et laisser sécher.

Alumine colorée

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atographie

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Ce tableau appelle les explications suivantes:

Ad 2 : Extraction du colorant de la solution ou suspension aqueuse.

2.1. a) On recommande d'extraire dans un tube à centrifuger. Pour séparer, on pipette le liquide surnageant et le transfère dans un autre tube, pour une deuxième extraction éventuelle (une extraction suffit dans la plupart des cas). On peut éventuellement laver la couche quinoléique avec de l'eau contenant un peu de tampon; on enlève cette eau de lavage et continue comme sous 3.

b) Il y a net avantage à travailler à un pH fixe, le même pour tous les cas, situé aux environs de 3, l'extraction et la séparation des couches étant meilleures. On a été amené à cette notion d'un pH fixe après avoir constaté que le pH des solutions de colorants purs diffère passablement d'un colorant à l'autre; c'est ainsi que des solutions $1/200M$, dans l'eau distillée, présentent les valeurs suivantes *:

bleu d'alizarine	3.72	violet de méthyle	4.65
chrysoïdine	4.40	phloxine P	6.28
tropéoline 000 No.1	6.55		

c) La quinoléine extrait également un grand nombre de colorants naturels. C'est un point dont il faut se souvenir au cours de l'analyse, mais qui ne semble pas présenter d'inconvénients, car beaucoup de ces colorants naturels (par ex. les anthocyanes et les flavones) sont fortement adsorbés par l'alumine et ne s'en laissent éluer que difficilement, contrairement aux colorants synthétiques.

2.3. On recommande de réduire au minimum la durée de contact des colorants avec les divers réactifs et de les amener en solution aqueuse concentrée ou sur alumine (*cf.* 3.2.) aussi rapidement que possible. Une fois les colorants sur l'alumine il est indiqué d'en faire l'examen chromatographique aussitôt que possible, pour empêcher leur oxydation éventuelle.

Ad 3 : Extraction du colorant de la solution quinoléique.

a) Le coefficient de partage de la plupart des colorants est, dans le système quinoléine-éther et eau, nettement à l'avantage de ce dernier dissolvant, d'où résulte une forte concentration du colorant dans le petit volume d'eau utilisé. Certains colorants, cependant, ont un coefficient de partage tel qu'il est difficile de les faire passer totalement dans l'eau. Dans ce cas, il faut traiter la phase quinoléine-éther avec de l'alumine hautement activée (selon 3.2). D'autres colorants ont la propriété de précipiter dans le système quinoléine-éther. Il faut alors centrifuger puis décanter prudemment la phase quinoléine-éther, en laissant dans le tube la solution aqueuse et le précipité. On dissout ensuite ce dernier en ajoutant un peu d'éthanol à 96 % et on obtient une solution limpide, prête pour l'analyse. On peut aussi diluer une petite quantité de la quinoléine colorée avec un peu d'éthanol et chromatographier ce mélange en ayant soin de faire un premier développement avec de l'éther, pour chasser la quinoléine, puis en séchant et développant avec un éluant approprié.

D'une manière générale il est recommandable de faire subir le même traitement au colorant de comparaison, et ceci tout particulièrement lorsque le colorant a dû être retiré de l'aliment à chaud, en présence d'acide chlorhydrique (c'est ainsi qu'on a constaté que l'érythrosine donne des chromatogrammes assez différents suivant qu'elle a ou n'a pas été traitée de cette façon).

b) Pour les essais d'extraction avec la quinoléine, on a examiné les colorants suivants:

Colorants jaunes : auramine O; jaune naphtol S; tartrazine; jaune acide R; jaune de quinoléine; chrysoïdine; orangé GGN; Sunset Yellow FCF.

Colorants oranges : orangé L; tropéoline OOO No. 1; ponceau SX; écarlate palatin GN.

Colorants rouges : éosine à l'alcool; rocelline; phloxine P; érythrosine; azorubine S; rouge solide E; ponceau R; ponceau 3R; éosine; fuchsine; fuchsine acide; nouvelle coccine; amaranthe; bordeaux BL.

Colorants bleus : bleu d'aniline soluble dans l'alcool **; indigocarmin; bleu d'alizarine; érioglaucine A; bleu soluble pur; induline.

Colorants violets : violet de méthyle B; violet cristal; violet acide 6B.

Colorants verts : vert malachite; vert lumière SF jaunâtre.

Colorants bruns : brun résorcine R; brun thiazine R.

Colorants noirs : nigrosine; noir profond (noir 5410); noir brillant BN; noir naphtol LT.

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* Mesures effectuées avec l'appareil Polymétron, à électrode de verre.

** On a rangé ce colorant parmi les hydrosolubles car, bien qu'il soit insoluble dans l'eau, sa solution alcoolique supporte une dilution considérable avec ce dissolvant.

II. IDENTIFICATION DES COLORANTS

L'identification des colorants est faite par *chromatographie sur plaque d'alumine*, par comparaison avec les colorants autorisés traités de la même façon et en recourant, le cas échéant, à des essais à la touche, à l'examen en lumière ultra-violette, *etc.*

a) Réactifs :

Alumine, hautement activée (voir sous Isolement des colorants).
Eluants : 1) mélanges d'eau, d'alcool absolu et de butanol normal.

Mélange I	eau 10 ml;	éthanol 10 ml;	*n*-butanol 90 ml
Mélange II	,, 20 ,,	, 20	80 ,,
Mélange III	,, 30 ,,	,, 40 ,,	,, 70 ,,
Mélange IV	,, 40 ,,	,, 40 ,,	,, 60 ,,
Mélange V	,, 50 ,,	,, 50 ,,	,, 50 ,,

2) mélanges d'alcool et d'eau: alcool à 80 %
alcool à 60 %.

Les mélanges ci-dessus (par ex. le mélange III) donnent également de bons résultats avec les colorants liposolubles couramment utilisés: soudan I, soudan G et annatto. Pour d'autres colorants liposolubles il peut être indiqué d'utiliser, dans l'ordre d'emploi et de pouvoir éluant croissant, la série: pentane, tétrachlorure de carbone, benzène, chloroforme, éther, acétone, alcool absolu et eau.

Pour les colorants hydrosolubles on pourra aussi utiliser, suivant les cas, d'autres mélanges encore, par ex. des mélanges acides ou alcalins.

b) Mode opératoire
1. Préparation des plaques

Prendre une plaque de verre (plaque B), par ex. de format 9 × 12 cm (d'anciennes plaques photographiques débarrassées de leur émulsion conviennent parfaitement) et y étaler, de manière aussi uniforme que possible, l'alumine. Cette condition doit être satisfaite pour obtenir de bons chromatogrammes et pour assurer, d'une plaque à l'autre, la fidélité des séparations. L'épaisseur de la couche d'alumine choisie est d'environ 0.5 mm. Pour préparer une plaque répondant à ces exigences il faut:

1 feuille de papier portant un arrêt constitué par ex. par un porte-objet collé à quelques centimètres d'un des bords, et

1 égaliseur, pour étendre l'alumine, constitué par ex. par une plaque de verre 9 × 12 cm (plaque A) ayant, dans la largeur, un bord bien rectiligne. Sur ce bord on fixe deux guides, épais de 0,5 mm, larges de 2 à 3 mm et distants d'environ 80 mm, de telle sorte qu'ils viennent reposer sur les bords de la plaque B (la plaque A est tenue à la main, verticalement, sur la plaque B); voir Fig. 1.

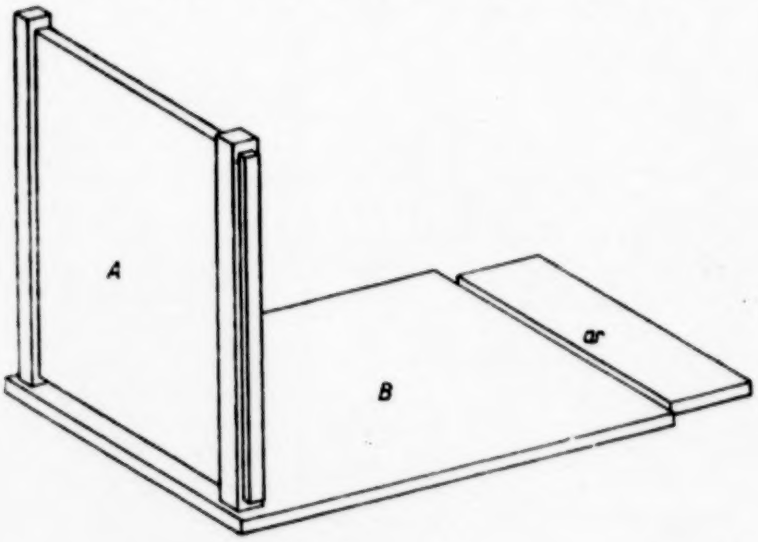

Fig. 1. Préparation de la plaque
A = égaliseur
B = plaque de verre sur laquelle on étale l'alumine
ar = arrêt

Des élastiques tendus autour de la plaque A, dans la longueur et sur les bords, donnent également de bons résultats comme guides.

Pour préparer la plaque B on la place sur la feuille de papier en l'appuyant contre l'arrêt. A l'autre bout de la plaque on dépose, sur toute sa largeur (sur ou contre elle), un petit tas d'alumine et étend celle-ci sur la plaque avec l'égaliseur *. Si la plaque d'alumine ainsi préparée présente des défauts (trous, raies, *etc.*) on les enlève en faisant passer l'égaliseur une deuxième fois, en présence d'un excès d'alumine. Remettre l'alumine non utilisée aussitôt dans le flacon.

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* en guidant avec le doigt le long de la plaque B.

2. *Chromatographie*

Au moment de l'examen chromatographique le colorant se trouve en solution ou adsorbé sur alumine. Il en découle deux techniques légèrement différentes.

a) Technique de la goutte

Déposer en ligne, à environ 1 cm d'un des bords de la plaque d'alumine (dans la largeur), au moyen de capillaires (une pipette ordinaire donnerait une goutte trop grosse) une série de gouttes, chaque tache correspondant à une des solutions à examiner. Le volume de solution à utiliser est de 10 à 30 μl environ et varie suivant la concentration de la solution en colorant et l'intensité de celui-ci. L'espacement des taches dépend de leur grandeur et doit être suffisant pour que les chromatogrammes ne se touchent pas; on peut faire ainsi de 6 à 8 chromatogrammes par plaque. On sèche ensuite les taches en portant la plaque à l'étuve pendant 3 minutes environ, à 104° C, puis passe à la chromatographie.

Dans le cas de colorants sensibles à la chaleur (contrôle possible avec 2 plaques, une avec taches séchées à 104° et l'autre avec taches séchées à l'air pendant une dizaine de minutes) il faut recourir à la technique de la poudre.

b) Technique de la poudre

Verser quelques gouttes de la solution aqueuse du colorant sur suffisamment d'alumine fraîche pour que la masse obtenue reprenne, après malaxage, sa consistance pulvérulente primitive. On peut prendre par ex. 0.8 à 0.9 g d'alumine et y ajouter 0.2 ou 0.1 ml de solution aqueuse. L'alumine peut contenir de 5 à 10 % d'eau sans changer d'aspect. Porter alors une pointe de spatule de cette poudre colorée sur la plaque d'alumine, à environ 1 cm du bord, et écraser doucement, avec la spatule, le petit tas formé.

Les alumines colorées obtenues dans l'isolement des colorants liposolubles et dans le traitement des mélanges quinoléine-éther colorés sont déposées de la même manière sur la plaque d'alumine.

On peut parfaitement avoir des plaques mixtes (ce cas se présente surtout pour les colorants liposolubles) portant des taches formées par des alumines colorées, provenant des graisses examinées, et par des gouttes des colorants de comparaison, en solution benzénique. La plaque doit être évidemment séchée avant le développement. Bien que cette technique ait donné de bons résultats il semble cependant préférable de ne comparer entre eux que des colorants traités de la même façon.

c) Développement

La plaque, préparée comme ci-dessus, est placée sous un angle de 15 à 20° dans un bac (par ex. un cristallisoir de 16-17 cm de diamètre, pour les plaques 9 × 12) qui est aussi légèrement incliné (environ 5°) et qui contient juste ce qu'il faut d'éluant pour mouiller 2 ou 3 mm de l'extrémité inférieure de la plaque (voir Fig. 2). On couvre ensuite et laisse monter l'éluant jusqu'en haut

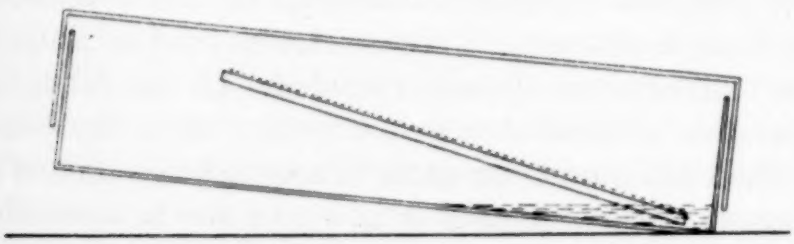

Fig. 2. Développement en cuve (coupe).

de la plaque, ce qui prend généralement 20 à 30 minutes; l'éluant doit monter régulièrement et former un front parallèle à la ligne des taches. On retire alors la plaque du bac et la sèche.

En général un développement suffit; cependant, lorsque la séparation des colorants est difficile on doit le répéter une ou plusieurs fois, après séchage(s) intermédiaire(s) de la plaque. On peut éviter ces répétitions et surtout ces séchages en travaillant à l'évaporation, c'est-à-dire à ciel ouvert, en rajoutant de temps en temps de l'éluant dans le bac. On peut aussi utiliser une lampe à infra-rouge et une cache appropriée pour ne chauffer qu'une bande horizontale au haut de la plaque. Enfin, il est également possible de combiner un développement lent avec l'évaporation, de préférence à la température ambiante (voir Fig. 3). C'est cette dernière variante qui donne les meilleurs résultats dans les cas difficiles.

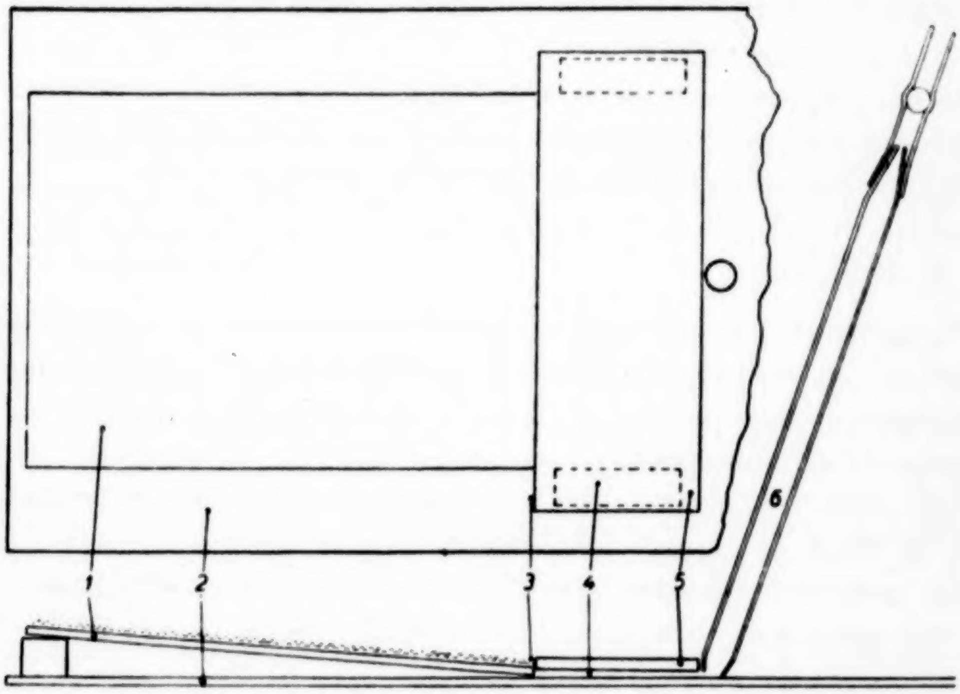

Fig 3. Développement lent avec évaporation:
1 = plaque avec alumine
2 = plaque de base
3 = pont d'alumine
4 = couvre-objet ou papier-filtre (l'épaisseur doit être telle qu'il se forme un film continu de dissolvant entre la plaque de base 2 et la plaque 5).
5 = plaque de verre sous laquelle se forme le film de dissolvant.
6 = pipette d'alimentation, inversée. L'orifice inférieur doit être assez grand pour permettre le passage des bulles d'air. La pointe est obturée par un tuyau de caoutchouc et une bille de verre.

d) Report des taches

Dans le cas de mélanges de plusieurs colorants on sépare le mélange sur une première plaque puis, le développement terminé, reporte chacune des zones colorées sur une plaque différente qui portera les colorants de comparaison de même couleur. Le cas échéant on fera un deuxième report, la comparaison n'étant sûre qu'en opérant dans des conditions aussi semblables que possible. Pour ces reports on sèche la zone colorée prélevée avec une spatule sur le chromatogramme encore humide et la porte sur la nouvelle plaque. Si le chromatogramme est déja sec, on prélève la tache en l'aspirant dans un tube de verre (diamètre = env. 6-8 mm) ayant à environ 1.5 cm de son extrémité un rétrécissement obturé avec un tampon d'ouate. En coupant l'aspiration la poudre tombe d'elle-même sur la plaque (voir Fig. 4).

Pour les colorants de comparaison on utilisera la technique de la poudre (voir ci-dessus).

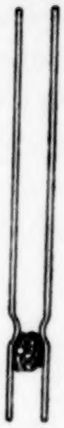

Fig. 4. Tube pour le report des taches.

e) Elution des taches

Si l'on désire procéder à un examen plus poussé du colorant comme par ex. déterminer son spectre d'absorption, son comportement à la réduction, *etc.*, il faut le remettre en solution. Dans ce but on prélève la tache complète sur le chromatogramme sec avec le tube décrit ci-dessus (voir Report des taches), mais on ne coupe l'aspiration qu'après avoir retourné le tube, pour empêcher l'alumine colorée de sortir. On branche ensuite le tube sur un flacon à vide de grandeur appropriée et on élue le colorant, comme on le ferait avec une colonne courante, avec 0.5 à 1 ml de dissolvant.

f) Sensibilité

Les quantités limites de colorants qu'on peut encore déceler avec certitude varient selon la teinte de ceux-ci, l'oeil n'ayant pas la même sensibilité pour toutes les couleurs. De toute façon la sensibilité de la méthode est grande, ainsi que le montrent les quelques exemples suivants:

Colorant	*Quantité de colorant encore décelable avec certitude*	
	Technique de la goutte	*Technique de la poudre*
Ponceau 3R	0.1 γ	0.5 γ
Bleu d'alizarine	0.1 ,,	1 ,,
Tartrazine	0.1 ,,	0.5 ,,
Soudan I	< 0.1 ,,	— ,,
Soudan G	< 0.1 ,,	— ,,

g) Identification

L'identification est basée sur la comparaison du R_F du colorant examiné avec ceux des colorants de référence ainsi que, le cas échéant, sur des réactions à la touche et l'examen en lumière ultra-violette. Ces diverses méthodes suffisent dans la plupart des cas, mais il va sans dire que d'autres examens peuvent encore être faits sur la solution du colorant, après élution de la tache, comme par ex. le comportement à la réduction, *etc.*

On a observé que le vert SF jaunâtre se décolore au cours du développement, ou peu de temps après ce dernier, sous l'influence de l'alcalinité de l'alumine. Il suffit d'exposer la plaque, humide ou non, au gaz chlorhydrique (par ex. dans un exsiccateur, en présence d'acide chlorhydrique concentré) pour voir réapparaître la couleur verte.

D'autre part, et pour mieux distinguer l'annatto du soudan G, il est indiqué de compléter l'examen chromatographique des colorants liposolubles par des réactions à la touche faites en déposant sur les taches, ou mieux contre elles, avec un capillaire, de l'acide sulfurique dilué (1:1) et du trichlorure d'antimoine en solution chloroformique.

Avec ces deux réactifs le soudan I donne une coloration rouge-violacé, le soudan G une coloration rouge-orangé et l'annatto une coloration bleue.

On a examiné ainsi 3 margarines et 31 graisses alimentaires du commerce, de marques différentes, et on a trouvé:

1. *pour les margarines*: 2 colorées avec de l'annatto et 1 avec du soudan G.
2. *pour les graisses*: 19 colorées avec un mélange de soudan I et de soudan G, 10 avec de l'annatto et 3 sans coloration artificielle.

h) *Fixation des chromatogrammes*

Les plaques d'alumine ne peuvent être aisément conservées telles quelles comme chromatogrammes de référence ou comme pièces à conviction. C'est pourquoi on a cherché à les fixer, sans altérer le colorant, avec une substance capable de pénétrer toute la masse de l'alumine et de la solidifier. Des solutions de collodion et d'acétate de polyvinyle n'ont pas donné satisfaction car seule la surface de l'alumine est fixée, l'intérieur restant pulvérulent. Le silicate de sodium n'a également rien donné de bon. Par contre la paraffine et l'alcool cétylique ont donné de bons résultats et peuvent être utilisés avec succès.

La paraffine est, en général, faiblement colorée en jaune; elle est aisément purifiée par agitation de quelques minutes, à chaud, avec de l'alumine hautement activée dont on la sépare ensuite par décantation. On prend une paraffine à bas point de fusion. Quant à l'alcool cétylique la qualité de la pharmacopée convient très bien. Pour la fixation on porte la plaque, bien sèche et inclinée comme pour le développement, dans un bac contenant l'agent de fixation fondu, en quantité juste nécessaire pour mouiller quelques millimètres de son bord inférieur, le tout étant placé sur un bain-marie ou, de préférence, dans une étuve réglée à 104° C environ. L'ascension de l'agent de fixation jusqu'en haut de la plaque prend un certain temps et est sensiblement plus rapide pour la paraffine que pour l'alcool cétylique. On retire ensuite la plaque du bac de fixation et la laisse refroidir: elle est alors fixée et peut servir de pièce à conviction.

CONCLUSION

Les nouvelles méthodes d'isolement et d'identification des colorants qui viennent d'être décrites ont donné d'excellents résultats dans la recherche d'une coloration artificielle des denrées alimentaires; leur simplicité, leur rapidité et leur efficacité font qu'on peut les recommander pour ce genre de travail.

RÉSUMÉ

Description d'une nouvelle méthode d'extraction, de séparation et d'identification des colorants artificiels pour denrées alimentaires, caractérisée par sa simplicité, sa rapidité et son efficacité.

Pour l'extraction des colorants liposolubles on se sert d'alumine, la substance à examiner étant dissoute dans un dissolvant de faible pouvoir éluant; pour les colorants hydrosolubles on utilise la quinoléine, en présence d'un tampon.

La séparation des colorants se fait par chromatographie sur ,,plaque" d'alumine et leur identification par comparaison avec les colorants de référence traités de même façon.

SUMMARY

Description of a new method for the extraction, separation and identification of the synthetic dyes used for colouring foodstuffs, characterized by its simplicity, its rapidity and its efficiency.

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The fat-soluble dyes are directly adsorbed on aluminium oxide after dissolving the substance to be examined in a solvent of weak eluting power; the water-soluble dyes are extracted with quinoline, in the presence of a buffer.

The dyes are separated by chromatography on aluminium oxide „plates" and identified by comparison with pure dyes treated in the same way.

ZUSAMMENFASSUNG

Es wird eine neue Methode zur Extraktion, Trennung und Identifizierung der künstlichen Lebensmittelfarbstoffe beschrieben, welche eine einfache, rasche und zuverlässige Arbeit gestattet.

Die fettlöslichen Farbstoffe werden direkt aus der in einem schwach eluierenden Lösungsmittel aufgelösten Substanz auf Aluminiumoxyd adsorbiert; die wasserlöslichen Farbstoffe dagegen werden in Gegenwart eines Puffers mit Chinolin extrahiert.

Die Farbstoffe werden mittels Chromatographie auf Aluminiumoxyd-„Platten" getrennt und durch Vergleichen mit gleichbehandelten reinen Farbstoffen identifiziert.

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THE ANALYSIS OF MONOCHLORACETIC ACID*

A PARTITION CHROMATOGRAPHIC METHOD

by

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INTRODUCTION

Monochloracetic acid is an important intermediate in the manufacture of several industrial chemicals. In particular, the hormone-type weedkillers 2,4-D, 2,4,5-T and MCPA are normally manufactured by condensation of the corresponding phenols with monochloracetate in alkaline solution. It is therefore advisable to have an accurate method of analysis for the determination of monochloracetic acid in the commercial product. The principal acidic impurities in commercial monochloracetic acid are the trichloro-, dichloro-, and unchlorinated acetic acids and glycollic acid. The trichloracetic acid content is usually only very small, but larger amounts of dichloracetic, acetic and glycollic acids are often present. Similar remarks apply to the impurities in commercial sodium monochloracetate.

Assay of monochloracetic acid has normally been confined to the non-specific estimation of "covalently-held" chlorine[1]. This method does not differentiate monochloracetate from dichloracetate. FRANKIEL AND ROMBEAU[2] have described a more rapid but equally non-specific method using the reaction with thioglycollic acid in alkaline solution. An empirical gravimetric method for the determination of monochloracetic acid in foods has been described; monochloracetate gives a crystalline precipitate with pyridine but dichloracetic acid and trichloracetic acid do not[3]. The polarography of halogenated acetic acids has been studied[4,5], but this does not indicate any promise of a reliable method for the determination of small quantities of dichloracetic acid and acetic acid in monochloracetic acid. Accepted methods[6] for estimation of dichloracetic acid in monochloracetic acid have been based on hydrolysis to glyoxylic acid followed by disproportionation in strong alkaline solution to give oxalate. This method was first described by POOL[7]; it is rather long and great care must be taken to avoid solubility and washing errors, and transference losses.

The problem, therefore, was the development of an accurate and reasonably rapid method for determination of small amounts of dichloracetic and acetic acids in commercial MCA. A semi-quantitative chromatographic method has been worked out by SMITH *et al.*[8] This method suffers from the use of empirical corrections to obtain quantitative results.

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EXPERIMENTAL

Experience has shown that the possibility of using partition chromatography on kieselguhr columns for certain separations may be predicted from simple partition experiments. Work was therefore directed to obtain suitable solvent pairs for separation. A literature survey showed that nitrobenzene would probably be a useful solvent for separating dichloracetic and monochloracetic acids. Preliminary work enabled us to separate these two acids using dilute sulphuric acid on kieselguhr as static phase and nitrobenzene as moving phase. Owing to the rather toxic nature of the solvent and to the fact that it proved difficult to reduce blanks to a low value, work was directed to discover a more suitable solvent.

Solutions of the two acids were made up in various organic solvents, previously equilibrated with the proposed static phase (usually dilute sulphuric acid). Aliquots of these solutions were titrated with sodium methylate solution using thymol blue as indicator. Further aliquots were shaken with equal volumes of static phase in stoppered test-tubes at room temperature for sufficient time for equilibrium to be reached. The layers were then allowed to settle, a known volume of organic solvent phase removed and titrated with sodium methylate as before. The approximate partition ratios were calculated from the pairs of titrations. Tables I-IV show the results obtained from some of the experiments with monochloracetic and dichloracetic acids. Table IV includes results for acetic acid.

TABLE I

Solvent pair: — chloroform: *N* sulphuric acid

Initial concentration of acid in solvent in g/l	*Partition ratios*	
	Monochloracetic acid	*Dichloracetic acid*
1	0.056	0.13
10	0.053	0.15

TABLE II

Solvent pair: — ether/benzene: 0.05*N* sulphuric acid

Initial concentration of acid in solvent in g/l	*% v/v benzene*	*Partition ratios*	
		Monochloracetic acid	*Dichloracetic acid*
1	2.5	3.0	20
10	25	1.9	8.8
1	25	2.0	8.3
1	50	1.2	4.8
1	75	0.6	1.9
1	92.5	0.28	0.7
10	100	0.022*	0.08*
1	100	0.016*	0.07*

* Using *N* sulphuric acid

TABLE III

Solvent pair: — *iso*propyl ether/benzene: *N* sulphuric acid

Initial concentration of acid in solvent in g/l	*% v/v benzene*	*Partition ratios*	
		Monochloracetic acid	*Dichloracetic acid*
10	0	1.3	13
1	0	1.3	13
1	25	1.0	12
1	75	0.4	3.7
1	50	0.8	8.7
10	50	0.8	8.2

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TABLE IV

Solvent pair: — *iso*propyl ether/petroleum ether BR 60-80° C: *N* sulphuric acid.

Initial concentration of acid in solvent in g/l	*% v/v Pet. Ether*	*Partition ratios*		
		Acetic acid	*Monochloracetic acid*	*Dichloracetic acid*
1	25	—	0.66	6.5
10	50	0.07	0.28	2.9
1	50	0.07	0.28	2.8
1	75	—	0.10	0.94
1	95	—	0.02	0.14

It was apparent from the start of the work that ethers were very good solvents to use, from the point of view that the ratio of partition ratios of dichloracetic: monochloracetic was of the order 10:1. Unfortunately ethyl ether is 'too good' a solvent for use in a chromatographic separation on an acidic column.

The two principal methods of reducing the partition ratio (solvent: static phase) in this case are (1) raising the pH of the static phase and (2) mixing a less favourable solvent with the ether. (1) is not desirable since dichloracetic acid is a stronger acid than monochloracetic acid, and hence, any increase in pH of the 'static phase' will tend to bring the apparent partition ratios of the acids closer together. Table II shows that about 70-90% v/v of benzene in ether would be suitable for a chromatographic separation. Unfortunately the ratio of the partition ratios is adversely affected by this proportion of benzene. By using a less favourable ethereal solvent, *iso*propyl ether instead of ethyl ether, less benzene needs to be added to obtain the right order of partition ratio for use on the column. Tables III and IV show the effect of petroleum ether (B.R. 60-80°C) and benzene on the partition ratios of the two acids from *N* sulphuric acid into *iso*propyl ether. A 50:50 mixture of *iso*propyl ether and petroleum ether was chosen as the most suitable moving solvent. It was considered that separation of the chlorinated acids from acetic acid would be easy on the column and this was confirmed by both simple partition experiments and chromatography. A few simple partition experiments showed that trichloracetic acid should accompany dichloracetic acid on the column. The partition ratio of glycollic acid is so heavily in favour of the aqueous phase that no interference need be expected.

Following previous experience with Hyflo super-cel columns of the type first used by MARTIN[9], chromatographic columns 1.4 cm diam. were packed with a static phase composed of 20 g Hyflo super-cel and 10 ml *N* sulphuric acid. The moving phase chosen from the partition experiments described above, gave a very satisfactory separation of dichloracetic and monochloracetic acids.

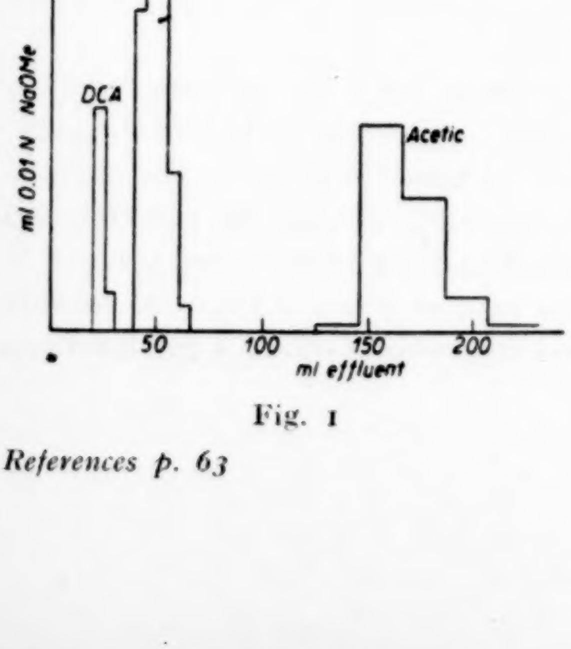

Fig. 1

The eluted solvent fractions were titrated under a stream of nitrogen with a 0.01*N* solution of sodium methylate in benzene using alcoholic thymol blue as indicator. Fig. 1 shows a typical elution curve relating volume of solvent eluted to methylate titres of individual fractions.

Some difficulty was experienced in obtaining a low blank value on the solvent eluted from the column. The trouble appeared to be due to acidic material being gradually leached from the kieselguhr, since the initially equilibrated solvent had a very low blank before passing through the column. The blank value was slowly reduced on passing large volumes of solvent through the column. The initial blank on a 15 ml fraction was 0.06-0.08 ml of 0.01*N* sodium methylate; this was reduced after 300-400 ml of solvent had passed to about 0.02 ml. Several different chemical treatments of the Hyflo super-cel before column packing were carried out in an attempt to reduce the blank. The only method found to be partially satisfactory was that in which the Hyflo was treated with dilute acid (equal weight) and refluxed with excess ether for 30 minutes. The slurry was then filtered and thoroughly washed with water until neutral. The Hyflo was sucked dry on the pump, and dried in the oven at 105-110° C for 24 hours. It was then prepared and packed into a column. The initial blank titres on 10 ml fractions were 0.01-0.02 ml 0.01*N* methylate. No simple method was found of reducing this blank to a lower value. This figure, however, is low enough to enable accurate and reproduceable determinations of the acids to be made. It was found necessary to extract acidic impurities from the technical grade *iso*propyl ether by initial washing with sodium hydroxide solution.

Apparatus

The chromatographic apparatus used consists of a glass tube 14 mm inside diameter and 50 cm long, provided with a constriction at one end and a B 19 socket at the other. The solvent reservoir is provided with a B 19 joint to mate with the column joint.

Titrations are carried out using a 10 ml burette calibrated in 0.02 ml. Estimations may be made to 0.01 ml which is the size of one drop of titrant. A fine glass jet serves to deliver a stream of CO_2-free nitrogen under the solution titrated.

Reagents

All reagents are of Analytical Reagent grade where available.

*Iso*propyl ether — technical grade
Petroleum ether — boiling range 60-80° C
Sodium hydroxide solution — approx. *N*
Sulphuric acid — *N*

Sodium methylate — 0.01*N:* — weigh about 0.6 g of bright metallic sodium, wash rapidly with 2 × 10 ml methanol. Then allow to dissolve in 100 ml methanol. When dissolved, dilute with a further 150 ml of methanol and add this mixture to 1,500 ml benzene through which a stream of nitrogen has been passed for some time ($\frac{1}{4}$-$\frac{1}{2}$ hour) to remove carbon dioxide. Store in an aspirator protected by a soda-asbestos guard tube. Standardize against pure monochloracetic acid.

Thymol blue indicator — 1 g/l in ethanol neutralized periodically with sodium methylate solution.

Equilibrated solvent (*S*) — mix equal volumes of *iso*propyl ether and petroleum ether and extract about 2 litres of the mixture with 2 × 100 ml of sodium hydroxide solution. Discard the aqueous layers and wash with 100 ml portion of water. Discard the water wash and equilibrate the solvent with 50 ml *N* sulphuric acid.

Supporting medium — mix the Hyflo super-cel* intimately with an approximately equal weight of *N* sulphuric acid. Reflux the mixture with a large excess of ether for 30-60 minutes. Cool and filter rapidly on a large Buchner funnel. Wash with copious amounts of water until the washings are neutral to bromocresol green indicator. Suck as dry as possible on the pump and dry the Hyflo on a flat dish at 105-110° C for 24 hours. Periodic stirring with a spatula helps to dry the Hyflo efficiently. Cool to room temperature.

Preparation of the column

Weigh 20 g of prepared Hyflo super-cel into a mortar. Add dropwise from a pipette with stirring, 10 ml of *N* sulphuric acid. Triturate gently but thoroughly to homogenize the Hyflo-sulphuric acid mixture. Add sufficient equilibrated solvent to form a thin slurry and mix well. Having plugged the bottom of the column with a small wad of ether-extracted cotton wool, pack the slurry into the column using MARTIN's[9] method with a perforated disc plunger. The length of a normal column is 24-28 cm. Wash through with about 50 ml of solvent *S* using an applied pressure, at 2.5-3 ml minute.

Procedure

(a) *Standardization.* Prepare a solution (A) of acids in *iso*propyl ether-petroleum ether containing approximately 20 g monochloracetic, 2 g dichloracetic, and 5 g acetic acids, per litre.

By applying nitrogen pressure to the top of the column, force the solvent carefully through the column until the surface of the solvent just reaches the surface of the packing. Carefully release the pressure and pipette 1 ml of solution A on to the surface. Gently apply pressure again to force the 1 ml into the packing. Release the pressure and wash the solution onto the column with 2 × 1 ml portions of equilibrated solvent *S*.

Pass equilibrated solvent through the column at a rate of about 2.5-3.0 ml minute by application of pressure to the top of the solvent reservoir. Collect 5 ml fractions in test-tubes and titrate each fraction with 0.01N sodium methylate under a stream of nitrogen. When the dichloracetic and monochloracetic acids have been eluted (see Fig. 1), collect 20 ml fractions and titrate in the same way until a constant blank value (usually 0.02-0.03 ml) is obtained. The position of the peaks gives an indication of where fractions should be collected.

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* Johns-Manville, Artillery Row, London.

(b) *Determination of unknown sample.* Dissolve about 2 g (W) of commercial MCA in equilibrated solvent and make up to 100 ml in a standard flask. Pipette 1 ml of this solution on to the column and wash on with 2 × 1 ml portions of solvents. Elute with solvent S at 2.5-3.0 ml min. Collect and tritate fractions as under *Standardization.*

When experience has been gained, larger fractions can be taken with ease in the following suggested manner.

Collect 5 ml fractions until the two dichloracetic acid fractions are titrated (after 20 ml). Following the next blank fraction, collect a suitable fraction (usually about 40 ml) indicated by the standardization to contain all the monochloracetic acid. Check the next 5 ml fraction as a blank and then collect 20 ml fractions until the acetic acid fraction is expected. Collect sufficient further solvent indicated by the standardization to contain all the acetic acid and titrate with sodium methylate. Check the next 5 ml fraction as a blank and then a fraction of the same volume as the acetic acid fraction. This should be used as the blank for the acetic acid fraction. The blank for monochloracetic acid is obtained similarly by titrating the appropriate volume of solvent.

The titre (t_D) of the dichloracetic acid is the sum of the two first large titres minus twice the blank on a 5 ml fraction (indicated in the first 3-4 5 ml fractions off the column).

The titre (t_M) of the monochloracetic acid is the difference between the titre of the first large fraction and the appropriate blank.

The titre (t_A) of the acetic acid is the difference between the titre of the second large fraction and the appropriate blank.

$$\%\ \text{dichloracetic acid} = \frac{12.9t_D}{W}; \quad \%\ \text{monochloracetic acid} = \frac{9.45t_M}{W}; \quad \%\ \text{acetic acid} = \frac{6t_A}{W}$$

Analysis of synthetic solutions

Synthetic solutions were prepared and analysed by the procedure described. Results are shown in Table V.

TABLE V

Solution No.	*Monochloracetic acid*		*Dichloracetic acid*		*Acetic acid*	
	mg added	*mg found*	*mg added*	*mg found*	*mg added*	*mg found*
I	20.73	20.55	0.61	0.61	0.38	0.38
	20.73	20.60	0.61	0.59	0.38	0.34
II	20.72	20.69	0.40	0.41	0.19	0.18
	20.72	20.82	0.40	0.35	0.19	0.18
III	20.74	20.63	1.03	1.03	0.38	0.35
	20.74	20.77	1.03	1.01	0.38	0.36
IV	20.71	20.55	0.19	0.17	0.96	0.93
V	20.75	20.62	1.24	1.23	0.97	0.93

Corrections are made in Table V for the amount of dichloracetic acid (about 0.8%) found in the AnalaR monochloracetic acid used for making up solutions. The amount of monochloracetic acid added was determined by direct titration of an aliquot of the solution used with sodium methylate; trichloracetic, acetic and glycollic acids being present in negligible amounts.

Slightly low results were obtained with small amounts of acetic acid (maximum error 0.05 ml 0.01 *N* sodium methylate) but correct results have been obtained with larger amounts, which are, however, not normally present in commercial monochloracetic acid.

The results indicate that the method is suitable for the accurate and rapid determination of monochloracetic acid in the commercial material.

Analysis of commercial SMCA

The sodium salt of monochloracetic acid (SMCA) is marketed commercially as a more convenient product to handle. Two techniques have been used for analysis of SMCA by this procedure.

(a) Dissolve a known weight of SMCA in dilute sulphuric acid. Mix a small aliquot of the resulting solution (normally 0.5 ml) with twice its weight of prepared Hyflo super-cel, carefully pack the whole mixture on the column and elute in the usual way. This method is quick and satisfactory if great care is taken to avoid transference losses during packing, but unless the sample portions of the Hyflo are removed after analysis, the characteristics of the column gradually alter with increased length.

(b) The preferred method, which is slower, is liquid - liquid extraction of the acids from acid solution with a solvent. Using a micro-extractor of the type described by WAYMAN AND WRIGHT[10], monochloracetic acid can be quantitatively extracted from acidified SMCA solutions with *iso*propyl ether.

Table VI shows figures for dichloracetic acid content obtained on some commercial samples of SMCA.

TABLE VI

Samples of SMCA	*SDCA content* *Manufacturer's specification*	*Found*
Manufacturer A	1.5% max.	3.0-4.5%
,, B	0.3% max.	1.4-1.8%
,, C	0.1% max.	0.3-0.6%

Since some discrepancy is evident, chromatography of a sample of commercial SMCA was repeated many times; the combined, titrated dichloracetic acid fractions were treated with concentrated sodium hydroxide to convert any dichloracetate to oxalate and glycollate. The oxalate found was precipitated as calcium oxalate and estimated on a semi-micro scale. The chloride liberated during hydrolysis of these fractions was also estimated and the results obtained are given below in terms of mg of SDCA.

(1) By alkalimetric titration with methylate — 17.2
(2) By precipitation as calcium oxalate and titration with permanganate — 17.0
(3) By volumetric chloride determination — 17.0

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These results indicate that the first fraction from this sample of commercial SMCA is substantially dichloracetic acid.

It is interesting to note that all commercial SMCA samples showed a trace (*ca.* 0.01%) of trichloracetate when tested semiquantitatively by Fujiwara's reaction. Trichloracetate is always estimated as dichloracetate by the present method.

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SUMMARY

A partition chromatographic method is described for the determination of dichloracetic, monochloracetic and acetic acids in commercial monochloracetic acid. A slight modification enables commercial sodium monochloracetate (SMCA) to be analysed. Analysis of a few samples indicates that some commercial SMCA samples contain slightly more dichloracetate than had been formerly supposed.

Once the column has been prepared and standardized a complete analysis can be carried out in under 2 hours. It is possible to use a column for 20-25 successive analyses.

RÉSUMÉ

Une méthode de chromatographie de partage est décrite pour le dosage des acides dichloracétique, monochloracétique et acétique dans l'acide monochloracétique commercial. Une légère modification permet d'effectuer l'analyse du monochloracétate de sodium (SMCA) commercial. L'analyse de quelques échantillons indique que certains SMCA commerciaux renferment légèrement plus de dichloracétate qu'on le supposait. Lorsque la colonne est préparée et étalonnée, une analyse complète peut être effectuée en 2 heures. Il est possible d'utiliser la même colonne pour 20-25 analyses successives

ZUSAMMENFASSUNG

Es wird eine Methode für Verteilungschromatographie beschrieben zur Bestimmung von Dichlor-, Monochlor- und Essigsäuren in Monochloressigsäure. Eine kleine Abänderung erlaubt das sich im Handel befindliche Natriummonochloracetat (SMCA) zu bestimmen. Die Analyse von einigen Mustern zeigt, dass gewisse sich im Handel befindliche SMCA etwas mehr Dichloracetat enthalten, als man vermutete. Wenn die Kolonne vorbereitet und geeicht ist, kann eine vollständige Analyse innerhalb 2 Stunden ausgeführt werden. Es ist möglich die gleiche Kolonne für 20-25 Analysen zu gebrauchen.

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THE USE OF RHODAMINE B IN ANALYTICAL CHEMISTRY

I. THE DETERMINATION OF SMALL QUANTITIES OF ANTIMONY

by

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The determination of microgram of antimony appears from the literature to have been somewhat neglected and no method suggested for the determination of inorganic antimony seems to be completely satisfactory. Most of the recent work on antimony has been connected with biological problems. Sandell[1] gives three methods, that of Webster and Fairhall[2] in which antimony is separated as stibine and determined with rhodamine B, the iodide method as outlined by McChesney[3] which may require a separate determination of any bismuth present, and the pyridine-iodide method of Clarke[4]. The rhodamine B method appears to be the most promising of these three and may eventually prove to be nearly specific. Another method recently published by Jean[5], in which antimony is determined as a methyl violet complex, also appeared to be promising. Jean[5] separates his antimony by the method of Clarke and Evans[6], who deposited antimony (in the absence of cupric ions) on electrolytic copper and stripped it off by washing with sodium peroxide. A number of polarographic methods for antimony have also been published[7-10], but these are not widely applicable owing to the complex polarographic characteristics of this element which have not been completely elucidated.

In most cases it is necessary to separate the antimony from the sample prior to the final determination. A number of methods are available but the most convenient appeared to be that introduced by Blumenthal[11] and elaborated by Kallmann and Pristera[12], *viz.* the coprecipitation of the antimony with manganese dioxide.

The combination of a manganese dioxide precipitation with a colorimetric finish does not appear to have been used previously to determine antimony, and accordingly in the present work the determination of antimony by methyl violet and by rhodamine B after concentration on a manganese dioxide precipitate was investigated.

For the rhodamine B determination of antimony it is necessary that the ion be present in the pentavalent state and oxidation is therefore the final step in any variation of the method prior to the addition of the reagent. Webster and Fairhall used ceric sulphate, but a better method was evolved by Maren[13] in which a sulphuric-nitric-perchloric acid mixture was used. The superiority of the latter has been confirmed by Freedman[14]. An earlier version of the method by Fredrick[15] has the disadvantage that bromine is used to bleach excess reagent and may cause difficulties; in addition, many ions interfere with this version of the method.

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EXPERIMENTAL

Our work has confirmed the details given by Maren and by Jean, and has shown that the conditions used by the former are directly applicable to the determination of antimony collected on a manganese dioxide carrier.

Since in the main the development of the various stages used in the present method are adequately covered in the literature, it is not necessary to give further details than those stated under the heading method. Any points of special interest are mentioned in the discussion.

The method has been checked for possible interference from a number of elements in the following manner. A suitable aliquot of standard antimony solution, together with a measured amount of solution of the element to be tested for interference, were placed in a beaker and carefully evaporated to dryness. Sulphuric acid was then added and the antimony prepared for determination as described in the method. By taking suitable aliquots of this prepared solution a calibration graph was constructed and compared with the calibration obtained for antimony alone. Where no difference was observed between the two graphs greater than that which could be attributed to the normal error of the method, it was considered that interference was negligible. The results are shown in Table I.

TABLE I

EFFECT OF IONS ON THE DETERMINATION OF ANTIMONY WITH RHODAMINE B

Constituent	*Added as*	*Level mg*	*Volume of reagent used in ml of 0.02 % solution*	*Effect*
Aluminium	Ammonium alum	1.0	5	None
		10.0	5	Variable recoveries of Sb
		10.0	10	None
Arsenic	Sodium arsenate	1.0	5	None
		10.0	10	None
Bismuth	Bismuth oxide	1.0	5	None
		10.0	10	None
		50.0	10	None
Chromium	Potassium dichromate	1.0	5	† Recovery of Sb very low Reagent oxidized
	Chrome alum	10.0	5	Loss of sensitivity
		10.0	10	Not significant
Cobalt	Cobalt sulphate	1.0	5	None †
		10.0	5	None †
Copper	Copper sulphate	10.0	5	None
Gold	Chloride solution	1.0	5	Behaves as Sb but solution more deeply coloured. Not pptd on MnO_2, however, so does not interfere with present method

Constituent	*Added as*	*Level mg*	*Volume of reagent used in ml of 0.02 % solution*	*Effect*
Iron	Ferric ammonium sulphate	1.0	5	None
		10.0	5	Sensitivity reduced to 80 % of normal
		10.0	10	None
Lead	Lead acetate	1.0	5	No interference, but precipitation of $PbCl_2$ at 10 mg level is troublesome
		10.0	5	
Manganese	Manganous sulphate	1.0	5	None on determination. During $HClO_4$ oxidation a deep violet appears, but on continued heating solution becomes colourless
		12.5	5	
		70.0	5	
Mercury	Mercuric chloride	10.0	10	Negligible
Nickel	Nickel sulphate	10.0	5	Negligible
Palladium	Palladium	10.0	10	None
Platinum	Platinum chloride 1% solution	1.0	10	Tends to give an extractable fluorescent complex similar to antimony
		10.0	10	
Silver	Silver nitrate	10.0	10	Some slight loss of reproducibility
Thallium	Thallium carbonate (dissolved in HNO_3)	1.0	10	Interferes seriously giving a similarly coloured extract to Sb but with intense red fluorescence
		10.0	10	
Tin	Stannous chloride	0.5	5	Slight loss of sensitivity
		0.5	10	None
		1.0	5	No reaction below 15 µg Sb 20 µg read as 10
		5.0	5	No antimony reaction None extracted
Titanium	Titanous chloride	10.0	5	† Recoveries low and variable
		10.0	10	Effectively same calibration as Ti free solutions, but colour of solutions slightly more red
Tungsten	Sodium tungstate	1.0	10	None
		10.0	10	No interference with Sb determ., but a white ppt. is obtained on adding H_2SO_4 prior to final turning. This did not re-dissolve
Vanadium	Vanadium pentoxide (dissolved in H_2SO_4)	1.0	5	† Small at lower levels but errors of reproducibility increase with increase of vanadium
		10.0	10	
Zinc		10.0	5	None

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† Various changes of colour occur during preparation of solutions for extraction.

METHOD

Reagents

Manganous sulphate solution, 5 %. Dissolve 12.5 g 'AnalaR' quality manganous sulphate in 250 ml water to which a few drops of nitric acid have been added.
Potasium permanganate solution, *1.25%*
Nitric acid, *1.2M*

Rhodamine B solution 0.04%.

Phosphoric acid, *1.0M.*

Constant boiling hydrochloric acid solution (ca. 5M) : Mix 250 ml of 'AnalaR' quality hydrochloric acid and 250 ml of distilled water and distil from a simple distillation apparatus. Reject the first 50 ml of distillate and collect the next 400 ml.

Standard antimony solution : Weigh out 0.5 g pure antimony metal powder into a beaker. Add 25 ml (18*M*) sulphuric acid and heat until all the antimony is dissolved. Dilute while still hot with 150 ml 25% sulphuric acid solution and cool. Transfer to a 250 ml graduated flask and make up to volume with 25% sulphuric acid.

Place 0.50 ml of the prepared solution in 100 ml graduated flask and make up to volume with 25 % sulphuric acid when:

$$1 \text{ ml} \equiv 10\ \mu g \text{ antimony}$$

Special apparatus

(1) A photoelectric absorptiometer with suitable cells and filters. In the present work a Spekker absorptiometer was used with a mercury vapour lamp, Ilford yellow-green filters and 1 cm cells.
(2) A simple hand-operated centrifuge.

PROCEDURE

'AnalaR' quality reagents should be used throughout unless otherwise stated.

1. Manganese dioxide precipitation

Weigh out an adequate quantity of sample, place in a 600 ml beaker, and add sufficient 8*M* nitric acid to dissolve the material. When solution is complete boil to remove all trace of nitrous acid. Cool and dilute to 200 ml with 1.2*M* nitric acid. (Notes 1 and 2.) Add 5 ml of 5 % manganous sulphate solution and heat to boiling. Add 2.5 ml of 1.25 % potassium permanganate solution dropwise and continue boiling for a further two minutes. Allow the solution to stand at a temperature of about 70° C for a further 30 minutes.

2. Preparation of test solution

Filter the solution from the manganese dioxide precipitation through an 11 cm Whatman No. 40 filter paper and wash three times with 10 ml portions of hot 1.2*M* nitric acid. The first two washings should also be used to free all adhering precipitate from the beaker. Completely dissolve the precipitate by allowing 10 ml of a hot 20:1 mixture of 1.2*M* nitric acid and 100 vol. hydrogen peroxide to run down the sides of the filter paper. Collect the filtrate in a 50 ml graduated flask. (The HNO_3/H_2O_2 mixture should be prepared by heating the nitric acid and carefully adding the hydrogen peroxide immediately before use.) Wash the funnel and filter paper first with 10 ml of the nitric acid-hydrogen peroxide mixture and finally with water. Collect the washings in the 50 ml flask. Cool the flask, mix well, and make up to the mark with water. This solution, referred to as the prepared olution, is now ready for antimony determination.

3. *Preparation for oxidation stage*

Pipette 5 ml (or other suitable volume) of the prepared solution into a clean 100 ml beaker. Carefully add 6 ml 18*M* sulphuric acid. Cover the beaker with a watch glass and heat on a hot plate until dense fumes of sulphur trioxide appear. Cool and rinse down the watch glass and sides of the beaker with a minimum of distilled water. Remove the watch glass and replace the beaker on a piece of asbestos paper on the hot plate. Continue heating, but do not allow the solution to boil, until fumes again appear. Transfer to the hot plate itself and heat until dense fumes appear freely. Heat for a further two minutes and cool. (Note 3.)

4. *Oxidation of antimony to the pentavalent state*

Add one drop of 16*M* nitric acid and three drops of 60 % perchloric acid. Mix thoroughly. Heat on the hot plate; the solution should become a deep purple. Continue heating until the colour fades and dense fumes are evolved. Heat for a further two minutes and cool. Rinse down the sides of the beaker with 4-5 ml of water and carefully mix the contents. Heat first on a piece of asbestos paper on the hot plate as before and then directly on the hot plate until dense fumes are evolved. Continue heating for a further two minutes and cool. This stage in which antimony is oxidized from the tetravalent to the pentavalent state is very critical. Traces of organic matter must be avoided. If it is suspected that oxidation is not complete, the above procedure should be repeated. If the beaker is allowed to go dry during the procedure a further 6 ml of 18*M* sulphuric acid should be added and the above procedure repeated; this should be avoided, however, as in this case results are usually low.

5. *Colorimetric determination of antimony*

Place the beaker in a bath of ice water and leave for 30 minutes. Place also sufficient amounts of hydrochloric acid, phosphoric acid and rhodamine B solutions and benzene in the ice bath and leave for 30 minutes. Keeping the beaker in the ice bath add 6 ml of the hydrochloric acid solution (some hydrogen chloride may be evolved but if the solutions are thoroughly cool the evolution should be small) and allow to stand for 5 minutes. Then add 8 ml of the phosphoric acid solution, mix and immediately add 5 ml of rhodamine B solution. Transfer to a 75 ml separating funnel containing 10 ml of benzene. Shake vigorously for 2 minutes. (Note 4.)

Allow the benzene layer to separate and transfer it to a 15 ml centrifuge tube and spin for 30 seconds. Place the cleared benzene solution in a test tube and close with a cork. The colour of the benzene solution should be purple-magenta. If the tint is brown or reddish the presence of nitric and/or perchloric acids is indicated and the determination must be repeated with more care in the oxidation stage.

Measure the absorbancy of the solutions using a Spekker absorptiometer with yellow green filters as follows: —

Pour the sample solution into a 1 cm cell, place in the light beam and zero in the usual way. Replace the sample solution by the blank solution and read off the absorbancy obtained.

It is recommended that not more than six determinations be carried out at any one time in order to minimize the time the benzene solutions are standing before reading.

The results obtained with the triplicate samples should agree within ± 10 %. If the divergencies are greater than this, failure at the oxidation stage is indicated and the procedure should be repeated from para. 3.

The amount of antimony present (a microg.) is read off from the calibration graph prepared as described below.

$$\text{Concentration of antimony in original sample} = a \times \frac{50}{b} \text{ p.p.m.}$$

Where b = the amount of prepared test solution used in para. 3, 5 ml is usually quite sufficient, and the normal value of b is therefore 5.

Note 1. Halides interfere with this precipitation. The material is preferably in the form of nitrate or oxide. If an halide it should be fumed down with slight excess sulphuric acid until completely converted to sulphate.

Note 2. A blank should also be prepared using a quantity of 8*M* nitric acid equal to that required to dissolve the sample and making up to 200 ml with 1.2*M* nitric acid. Treat the blank in the same way as the sample throughout.

Note 3. This procedure removes all trace of hydrogen peroxide. If the solution becomes dark in colour organic matter has been introduced and the determination must be rejected. To save time it is recommended that the above process and the succeeding oxidation is performed in triplicate.

Note 4. The cooling of all reagents and sample ensures that the final solution will be below 20° C in spite of the heat of dilution of the sulphuric acid.

6. *Preparation of the calibration graph*

The points on the graph should be determined in duplicate.

Place 0, 0.5, 1.0, 1.5, 2.0 and 2.5 ml of the standard antimony solution in six 100 ml beakers using a semimicro burette. Treat as described for the prepared test solution, paragraphs 3-5 above.

The purple colour which appears during the oxidation stage (para. 4 above) will not occur in this instance as manganese is absent. Instead, the solutions take on a transient yellow colour due to the decomposition of perchloric acid. The fuming must be continued for two minutes after this colour has faded.

When measuring the absorbancies, the solution containing no antimony is used as the blank.

The graph obtained by plotting absorbancy against antimony concentration is normally a straight line and is suitable for amounts of antimony up to 25 μg.

RESULTS AND DISCUSSION

Recoveries obtained with the method both from water solutions and from common salts are shown in Table II. Antimony was always added as standard solution (see method). The salts were dissolved in water before addition of antimony.

TABLE II

RECOVERY OF ANTIMONY FROM SOLUTIONS OF WATER AND SALTS

Antimony added	*Antimony recovered*	*Solution*	
5	6.0	Water	
10	9.8	Water	
	12.0	K_2SO_4	
15	13.0	Water	
	16.5	K_2SO_4	
20	19.2	Water	
	18.0	Water	
	20.0	Water	
	18.0	Water	
	19.0	Water	
	21.0	K_2SO_4	
	17.0	HNO_3	I.M.
	19.2	$NaNO_3$	
	19.4	NaCl	
25	24.0	Water	
	24.0	Water	

These results show the expected reproducibility of most colorimetric procedures, giving results which appear to be within an order ± 10 % of the true value.

The main difficulty of the method is the oxidation stage, and for satisfactory results strict attention to quantities of reagents and experimental technique is required. Thus, in particular, the oxidation mixture of nitric and perchloric acids must be added to a fuming sulphuric acid solution, otherwise the oxidation is uncertain. Since nitric acid, even in minute amounts, attacks the rhodamine B, care must be taken that no nitric acid is left when proceeding to the colorimetric finish of the method.

Although the colorimetric procedure offers no difficulty, strict attention to quantities of reagent is required. In particular, the concentrations of hydrochloric and phosphoric acids used are important. Too little hydrochloric acid, as noted by MAREN, leads to low or zero results. The use of phosphoric acid to minimize interference from iron was introduced by MAREN and it has been found to have a beneficial effect in the presences of other substances. American methods use 8 ml of $3N$ or $3M$ phosphoric acid, a threefold difference, and stress the bleaching effect of too high concentrations of this acid; the fact that fading also occurs if solutions are allowed to stand for more than a few minutes after addition of phosphoric acid prior to extraction of the antimony complex with benzene is also stressed. Our experiments have confirmed these observations. The present method uses 8 ml of $2M$ phosphoric acid as being an optimum amount.

5 ml of 0.02 % rhodamine B is used by MAREN. This is adequate and gives good results in the case of pure solutions of antimony. In the investigation of interferences, however, we have noted a number of elements in which interference is only apparent; this is due to the fact that the element complexes with rhodamine B in preference to the antimony; in most cases, however, the subsequent complex does not extract with benzene under the same conditions as the antimony. Hence, if sufficient reagent is present to combine with the antimony after the interfering element has been completely complexed, the former can readily be extracted and determined.

It was hoped that the combination of manganese dioxide precipitation with the subsequent extraction and determination of the antimony with rhodamine B would give a specific method for this element, but the results so far have only been partially successful.

Including those elements tested by MAREN[13] and WEBSTER AND FAIRHALL[2] some thirty-eight elements have been investigated for interference with the method; of these only gold, platinum and thallium give a colour with rhodamine B extractable in benzene. Tin, tungsten and vanadium give complex with rhodamine B but these are not extracted by benzene, and provided enough reagent and HCl is used their interference can be eliminated when they are present in moderate amounts.

Of the three elements forming extractable complexes, gold is not carried down on manganese dioxide, and platinum does not cause serious error to the method if the amount present is not in excess of one milligram.

Thus by combining manganese dioxide precipitation with the colorimetric finish we have a method which appears to be specific for antimony except in the presence of thallium which, even in small amounts, can be detected by the strong red fluorescence it imparts to the benzene extract.

Why gold, thallium and antimony should be the only elements to form extractable complexes with rhodamine B is not at present known; it is doubtless bound up with the mechanism by which the complex is formed and the nature of the metal ions involved. We hope to elucidate this problem in further investigations.

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The absorption curve for the complex plotted on a Unicam spectrophotometer is similar to that obtained by MAREN[13]. except that the peak at 5650A is somewhat sharper and there is indication of another small and broad peak about 5300A.

The method recently put forward by JEAN[5] has been tested by us and found to have a reasonable sensitivity. The attraction of this method is the oxidation with sodium nitrite, but unfortunately antimony in the tetroxide form is not oxidized to the pentavalent state by this method and we have not therefore proceeded with it.

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SUMMARY

A method for determining antimony is given. The antimony is separated from other ions by collection on a manganese dioxide precipitate which is redissolved. After oxidation to the pentavalent state the antimony is determined with rhodamine B. In the absence of thallium and large amounts of platinum or vanadium the method appears to be specific.

RÉSUMÉ

Une méthode de dosage de l'antimoine est proposée. L'antimoine est séparé des autres ions en le recueillant sur un précipité de dioxyde de manganèse que l'on redissout ensuite. Après oxydation à l'état pentavalent, l'antimoine est dosé par la rhodamine B. En l'absence de thallium et de fortes teneurs en platine ou en vanadium, la méthode est spécifique.

ZUSAMMENFASSUNG

Es wird eine Methode vorgeschlagen, um das Antimon zu bestimmen. Das Antimon wird von den andern Ionen getrennt, indem man es auf einem Niederschlag von Mangandioxyd gewinnt, welchen man nachher auflöst. Nach der Oxydation zur Wertigkeit 5 wird das Antimon mit Rhodamin B bestimmt. In Abwesenheit von Thallium und grossen Gehalten an Platin oder Vanadium ist die Methode speziefisch.

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THE HETEROMETRIC MICRODETERMINATION OF MERCURY WITH MERCAPTOBENZTHIAZOLE IN THE PRESENCE OF AN EXCESS OF FOREIGN METALS

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INTRODUCTION

In a previous investigation[1] the conditions necessary for the determination of mercury in acidic, neutral or alkaline solution were given. In this paper we deal with the same determination but in the presence of large excesses of foreign metals. The amount of mercury required for the analysis remains the same ($\sim 5 \cdot 10^{-4} M$, or $\sim$ 2 mg Hg in 20-30 ml solution). In the presence of many cations, especially in the presence of trivalent cations the maximum density values obtained are lower than in the blank but nevertheless, the determination of mercury can be carried out without difficulty and the error in general lies between zero and 3 %. Except in the presence of copper and bismuth, the mercury could be determined directly without making use of complexing agents. An aqueous solution was used which had been acidified with acetic acid. In most cases the mercury content in the foreign metal could be reduced to less than *one* percent of the total metal content and there was no limit to the amount of foreign metal which could be present. Each titration took, on the average, 20-30 minutes. Special consideration was given to the determination of mercury in the presence of excesses of copper or bismuth, for which methods were elaborated which permitted a precise determination of mercury in the presence of $\sim$ 98 % of the former metals.

EXPERIMENTAL

The same instruments and the same working conditions were used as in the previous investigations[2]. All chemicals used were either analytical reagents or chemically pure reagents. The titrations were carried out at 20° C.

RESULTS AND DISCUSSION

(1) *Determinations in the absence of complexing agents*

Table I gives a compilation of titrations which were carried out in acetic acid water solution. The composition and the results are given in the table. No filter whatsoever was used, even in the presence of strongly coloured solutions. This was possible so long as the coloured cation did not participate in the reaction. The titration time remained the same as in the absence of foreign metals.

TABLE I

Composition: 5 ml 0.002*M* $Hg(NO_3)_2$ + 1 ml *M* CH_3COOH + 14 ml complements + *x* ml 0.0066*M* mercaptobenzthiazole (alc.).
Content: 2.006 mg Hg. Temp. = 20° C

Exper. number	*x = ml*	*Complements*	*% Hg*	*Titration time in min*	*Initial precip. at ml*	*Max. density value*	*% error*
1	3.1	1 ml *M* $Ca(NO_3)_2$ + 13 ml H_2O	4.8	15	0.4	0.32	+3.3
2	2.98	4 „ „ „ + 10 „ „	1.2	35	0.0	0.39	—0.6
3	3.00	1 „ „ $Ba(NO_3)_2$ + 13 „ „	1.4	19	0.2	0.32	0.0
4	2.97	4 „ „ „ + 10 „ „	0.36	27	0.2	0.34	—1.0
5	2.95	1 „ „ $MgSO_4$ + 13 „ „	8.0	12	0.2	0.43	—1.7
6	3.00	4 „ „ „ + 10 „ ,	2.02	28	0.2	0.46	0.0
7	3.10	1 „ „ $Zn(NO_3)_2$ + 13 „ „	3.0	19	0.2	0.59	+3.3
8	2.96	4 „ „ „ + 10 „ „	0.76	20	0.2	0.65	—1.3
9	2.93	1 „ „ $MnSO_4$ + 13 „ „	3.5	20	0.4	0.40	—2.2
10	3.04	4 „ „ „ + 10 „ „	0.9	12	0.0	0.62	+1.3
11	3.00	1 „ „ $Ni(NO_3)_2$ + 13 „ „	3.3	20	0.0	0.73	0.0
12	3.00	4 „ „ „ + 10 „ „	0.85	17	0.0	0.59	0.0
13	3.00	1 „ „ $Co(NO_3)_2$ + 13 „ „	3.3	21	0.0	0.69	0.0
14	2.95	4 „ „ „ + 10 „ „	0.84	29	0.0	0.41	—1.7
15	2.90	2 „ 0.5 *M* $Al(NO_3)_3$ + 12 ml H_2O	6.9	19	0.4	0.28	—3.3
16	3.10	2 „ „ „ $Cr(NO_3)_3$ + 12 „ „	3.7	18	0.4	0.34	+3.3
17	3.03	2 „ „ „ FeIII $NH_4(SO_4)_2$ + 12 ml H_2O	3.5	20	0.0	0.40	+1.0
18	3.00	1 „ *M* $Cd(NO_3)_2$ + 13 ml H_2O	1.8	28	0.3	0.63	0.0
19	2.95	4 „ „ „ + 10 „ „	0.44	45	0.2	0.42	—1.7
20	3.00	1 „ „ $Pb(NO_3)_2$ + 13 „ „	1.0	27	0.4	0.48	0.0
21	3.02	2 „ „ „ + 12 „ „	0.48	32	0.2	0.34	+1.2

TABLE II

Composition: 5 ml 0.002M $Hg(NO_3)_2$ + 15 ml (or 25 ml) Complements + x ml 0.0066M mercaptobenzthi (= MBT) alc.

Exp. number	*pH*	*MBT x ml*	*Complements*
22	∼3.0	3.02	3 ml M CH_3COOH + 1 ml 0.2M $Cu(NO_3)_2$ + 3 ml 0.2M EDTA-Na_4 + 8 ml
23	∼7.0	>3.8	1 ,, ,, CH_3COONa + 1 ml 0.2M $Cu(NO_3)_2$ + 3 ml 0.2M EDTA-Na_4 + 10
24	∼9.5	2.98	1 ,, 2M NH_4NO_3 + 1 ml 2M NH_3 + 2 ml M Na_3-citrate + 1 ml 0.5M $Cu(NO_3)_2$ + 10 ml
25	∼9.5	3.03	2 ,, M NH_4NO_3 + 2 ml M NH_3 + 2 ml M Na_3-citrate + 1 ml 0.5M Cu(NO + 5 ml alc. + 3 ml H
26	∼9.5	∼3.2	2 ,, ,, ,, , + 2 , ,, ,, + 4 ,, ,, Na_3-citrate + 2 ml 0.5M Cu(NO + 5 ml
27	∼9.5	3.00	2 ,, ,, ,, + 2 ,, ,, ,, + 4 ,, ,, Na_3-citrate + 2 ml 0.5M Cu(NO + 5 ml
28	∼9.5	2.99	2 ,, ,, ,, + 2 ,, ,, ,, + 4 ,, ,, Na_3-citrate + 2 ml M $Cu(NO_3)_2$ + 5 ml
29	∼9.5	2.94	2 ,, ,, ,, + 2 ,, ,, ,, + 4 ,, ,, Na_3-citrate + 2 ml M $Cu(NO_3)_2$ ml alc. + 10 ml H_2O (vol. =
30	∼9.5	2.97	2 ,, ,, ,, + 2 ,, ,, ,, + 4 ,, ,, Na_3-citrate + 2 ml M $Cu(NO_3)_2$ 10 ml alc. + 5 ml H_2O (vol. =
31	∼9.5	2.97	2 ,, ,, ,, + 2 ,, ,, ,, + 4 ,, ,, Na_3-citrate + 2 ml M $Cu(NO_3)_2$ 15 ml alc. (vol. = 3
32	∼3.0	3.07	3 ,, ,, CH_3COOH + 3 ml 0.1M EDTA-Na_4 + 2 ml 0.1M $Bi(NO_3)_3$ + 7 ml
33	∼3.0	3.08	5 ,, ,, ,, + 4 ,, ,, ,, + 5 ,, ,, ,, + 1 ,,
34	∼7.0	2.97	2 ,, ,, CH_3COONa + 5 ,, ,, ,, + 5 ,, ,, ,, + 3 ,,

In some cases (Ca, Ba, Al, Cr) the maximum density value is reduced. The influence of the concentration of the foreign metal is not always observed and in these cases the concentration of the foreign metal may be even more than shown in the table. In other cases a lower density value is obtained with the higher salt concentration. In the presence of trivalent cations, the concentration of the foreign cation must be greatly restricted. The limits are given in experiments 15-17. As can be seen from the table, the heavy foreign metals (Pb, Ba, Cd) may comprise >99.5 %, the metals Co, Ni, Mn, Zn, > 99 %, and the light metal Mg, 98 %, of the total metal content. For the trivalent metals, aluminium may comprise more than 90 % while iron and chromium may make up more than 95 % of the total metal content.

(2) *Determination in the presence of excess bismuth*

(a) *In the presence of ethylenediaminetetraacetate.* Special heterometric titrations with bismuth and MBT were carried out in the presence of EDTA-Na_4 in order to clear up the pH-dependency of the precipitation. One experiment had the following composition: 5 ml 0.002M $Bi(NO_3)_3$ (+ HNO_3) + 1 ml 0.1N HCl + 2 ml M CH_3COOH + 2 ml M NH_4NO_3 + 3 ml 0.01M MBT + 2 ml 0.01M EDTA-Na_4 + 5 ml H_2O + x ml N NaOH. The result was that bismuth remained in solution at all pH's and no precipitation occurred. An analogous experiment which was carried out in the *absence* of EDTA-Na_4 showed that bismuth is precipitated heterometrically in acid solution. From our previous investigation[1] we know that EDTA, if present in acetic acid or sodium acetate nt: 2.006 mg Hg T = 20° C

Remarks	*% Hg*	*Titration time in min*	*Initial precip. at ml*	*Maximum density value*	*% error*
	12.7	30	0.4	0.93	+0.7
	12.7	32	2.0	∞0.80	
p max. then steep drop.	6.1	12	0.4	0.63	—0.7
imum, then drop.	6.1	15	0.0	0.96	+1.0
recipitate floats on the surface	3.06	25	0.4	∿0.60?	
	3.06	11	0.0	0.69	0.0
im line, then slow drop.	1.55	20	0.0	0.71	—0.3
„ „	1.55	15	0.0	0.75	—2.0
„ „ „ „ „	1.55	14	0.4	0.79	—1.0
„ „ „ „ „	1.55	15	1.4	0.53	—1.0
	4.6	35	0.0	0.94	+2.3
	1.92	45	0.2	0.81	+2.5
	1.92	30	1.8	0.89	—1.0

solutions, does not influence the heterometric titration of mercury with MBT. Acting on these results, we tried to determine mercury in acetic acid solution in the presence of bismuth, by the addition of EDTA-Na_4. Table II, experiments 32-34 (Fig. 1) show these results. The experiment number and the curve number correspond to facilitate

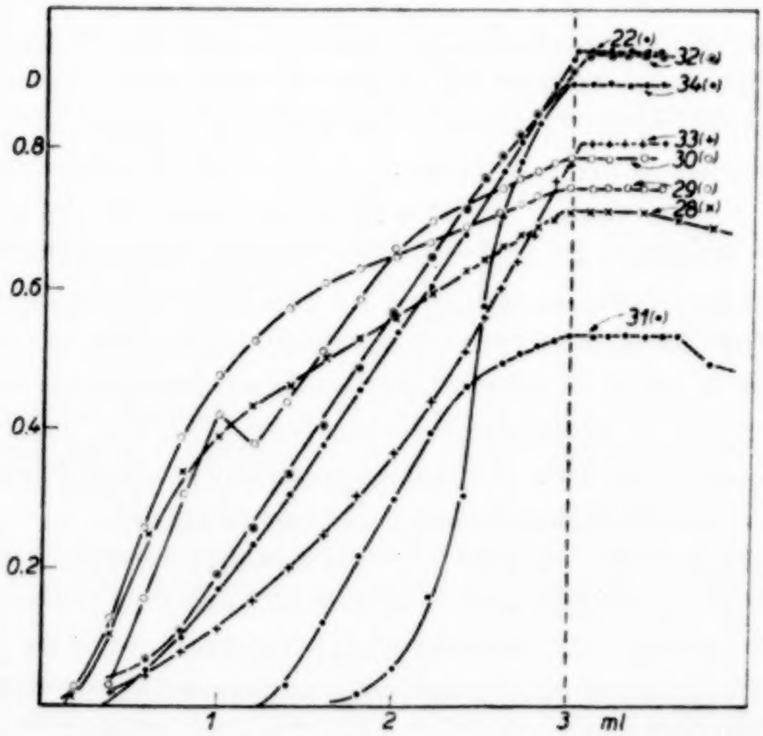

Fig. 1. Titrations of mercuric nitrate in solutions containing complexing agents and copper or bismuth.

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comparison. As can be seen, mercury can be determined without any difficulty in an acetate or acetic acid solution which contains sufficient EDTA to bind any bismuth. As experiment 34 with *sodium acetate* shows, the initial precipitation occurs very late, only after the addition of 60 % of the MBT which was necessary for the titration. This is of course a disadvantage, but in spite of this the obtained maximum density value was as high as usual and the error was only 1%. Our solution contained 98 % bismuth. Because of the maximum density values in the presence of EDTA and bismuth which are high, even less mercury can be determined.

(b) *In the presence of trisodiumcitrate.* In the presence of excesses of citrate, in neutral or alkaline solutions, a precipitate was obtained with bismuth immediately, and no titration could be made.

3. Determinations in the presence of excess copper

(a) *In the presence of ethylenediaminetetraacetate.* Just as in the case of bismuth, similar parallel heterometric and pH-titrations were carried out with copper in the presence, as well as in the absence of EDTA. We could ascertain that copper is not precipitated by the addition of MBT in the presence of EDTA under any conditions of pH's. We used this property for the heterometric titration of mercury in the presence of copper. Table II, experiments 22 and 23 (Fig. 1) show the results of such titrations from acetic acid or acetate solutions. As can be seen, mercury can be determined only in *acetic acid* solution if sufficient EDTA is added to bind the copper.

(b) *In the presence of trisodiumcitrate.* From our previous investigations we know that trisodiumcitrate does not interfere with the heterometric determination of mercury with MBT at any pH, and may be present in any concentration. From other investigations[3] we know that copper forms a soluble very strong complex with citrate, *especially in alkaline solution.* Acting on these results, we carried out a series of heterometric titrations some of which are compiled in Table II. The course of the titrations can be seen in Fig. 1. As experiment 24 shows, the titration cannot be carried out without disturbances if an *aqueous* solution of mercury is titrated. A minimum amount of alcohol must be present. As Fig. 1 shows, we obtain, in all cases, at the analytical end-point, an optical maximum density *line* and then the density drops with the further addition of MBT. The critical end-point is obtained by the intersection of the last part of the titration *line* with the horizontal maximum density line. As experiments 29-31 (vol. = 30 ml!) show, even a ∿ 30 % alcohol (by volume) does not change the value of the maximum density. In 50 % alcoholic solution (exp. 31), the maximum density value is already reduced. Apart from this, the initial precipitation only begins after the addition of 50 % of the MBT, which was necessary for the titration.

There is no limitation to the amount of trisodiumcitrate which may be present. This depends on the amount of alcohol added, as the solubility of trisodiumcitrate decreases with the addition of alcohol. The amount of copper which may be present on the other hand, depends on the amount of citrate and cannot be higher than 1:1. In any case, the mercury makes up less than 2 % of the total metal content. The titration proceeds without difficulty and lasts 10-20 minutes. The error lies between zero and 2 %.

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METHOD

1. General method

20 ml of an aqueous salt solution which contains 1 ml M acetic acid and about 2 mg mercuric mercury as nitrate or sulphate, are titrated heterometrically with an alcoholic solution of $0.01M$-$0.005M$ mercaptobenzthiazole.

The solution may contain the following cations, in a concentration of $0.2M$ or higher, as nitrates or sulphates: Ca, Ba, Mg, Zn, Mn, Ni, Co and Cd. Lead may not be at a concentration higher than $0.1M$. The concentration of the trivalent cations Al, Cr, Fe, may not be higher than $0.05M$.

No coloured filter is needed in the presence of coloured cations. The error is 0-3 %.

2. Determination in the presence of excesses of bismuth or copper

In the presence of ethylenediaminetetraacetate. (a) 20 ml of the aqueous solution of mercuric nitrate to be analysed, contain 1-2 mg mercury and an excess of bismuth which may constitute $\gtrsim 98$ % of the metal content. Sufficient ethylenediaminetetraacetate salt solution to bind the bismuth is added to the solution, The free strong acid which is present in solution is then transformed into acetic acid by the addition of sodium acetate, which may be present in excess. The solution is brought to a volume of about 20 ml and titrated heterometrically with an alcoholic solution of $0.01M$-$0.005M$ mercaptobenzthiazole.

An enlarged curve of the last part of the titration is drawn. The end-point is obtained from the intersection of the line of the last part of the titration with the horizontal optical maximum density line. The titration time is about 30-40 minutes. Error 0-3 %.

(b) The aqueous solution of mercuric nitrate or sulfate to be analysed contains 1-2 mg mercury and an excess of copper. To this solution is added sufficient ethylenediaminetetraacetate salt solution, to bind the copper. The solution obtained is neutralised and then 3 ml M acetic acid is added, since the final solution has to be acidic. The final solution is then brought to a volume of 20-30 ml and titrated heterometrically with an alcoholic solution of $0.01M$-$0.005M$ mercaptobenzthiazole.

The end-point of the titration is obtained from an enlarged curve of the last part of the titration by the intersection of the titration line with the horizontal optical maximum density line. No coloured filter is required. The titration time is $\sim$ 30 minutes. Error 1-2 %.

In the presence of trisodiumcitrate. (c) To the analysed solution which contains $\leqslant$ 2 mg mercuric mercury and an excess of copper (up to 98 % or more), are added: x ml M Na^{-3}-citrate + 2 ml M NH_4NO_3 + 2 ml M NH_3 + 5-10 ml alcohol. The solution is brought to approximately 30 ml and then titrated heterometrically with an alcoholic solution of $0.01M$-$0.005M$ mercaptobenzthiazole from a microburet (0.01 ml).

The minimum amount of trisodiumcitrate which has to be added is 1 mole citrate per 1 mole copper. The percentage of alcohol in the solution must be 15 %-30 %.

The end-point is obtained by the intersection of the line of the last part of the titration with the horizontal endline. No colour filter is needed. The titration lasts 10-15 minutes. Error 0-2 %.

From the two methods presented the last is to be preferred as the concentration of copper may be high and the titration proceeds quickly.

SUMMARY

1. A general method is presented for the determination of 1-2 mg mercuric mercury, in the absence of complexing agents, in 20 ml solution, with an error of 0-3 %.

The solution may contain: Ca, Ba, Mg, Zn, Mn, Ni, Co or Cd as nitrate of sulphate in a concentration of $0.2M$. The concentration of Pb should be $<0.1M$ and that of Al, Cr or Fe $\leqslant 0.05M$.

2. A special method is presented for the determination of mercury (1-2 mg Hg in 20 ml) in the presence of large excesses of bismuth ($\gtrsim 98$ %) by using ethylendiaminetetraacetate. Error 0-3 %.

3. A method is presented for the determination of mercury in excesses of copper in an acetic acid solution which contains ethylendiaminetetraacetate.

4. A special method is presented which permits the determination of 1-2 mg mercury in 30 ml solution which contains large excesses of copper (up to 98% or more). The titration is carried out in an alkaline solution of trisodiumcitrate. The titration proceeds rapidly. Error 0-2%.

RÉSUMÉ

1. Une méthode générale est proposée pour le dosage du mercure(II) (1 à 2 mg dans 20 ml de solution), avec une erreur de 0-3%, en l'absence d'agents complexants. La solution peut contenir Ca, Ba, Mg, Zn, Mn, Ni, Co ou Cd (sous forme de sulfates ou de nitrates) en concentration $0.2M$. La concentration en plomb doit être plus petite que $0.1M$ et celle d'Al, Cr ou Fe plus petite que $0.05M$.

2. Une méthode spéciale est proposée pour le dosage du mercure (1-2 mg dans 20 ml solution), en présence d'un gros excès de bismuth, ($\gtrsim$ 98%), en employant l'éthylènediaminetétraacétate. L'erreur est de 0-3%.

3. Une méthode est proposée pour le dosage du mercure en présence de cuivre en excès, en solution d'acide acétique, renfermant l'éthylènediaminetétraacétate.

4. Une méthode spéciale est proposée pour le dosage de mercure (1-2 mg dans 30 ml solution) en présence d'un gros excès de cuivre (>98%). Le titrage est effectué en solution alcaline de citrate trisodique. Ce dosage est rapide. L'erreur est comprise entre 0-2%.

ZUSAMMENFASSUNG

1. Eine allgemeine Methode wird vorgeschlagen, welche erlaubt, 1-2 mg Quecksilber in 20 ml Lösung in Abwesenheit von komplexierenden Körpern, mit einem Fehler von 0-3% zu bestimmen. Die Lösung kann enthalten $0.2M$ Nitrat oder Sulfat von Ca, Ba, Mg, Zn, Mn, Ni, Co oder Cd. Die Pb-Konzentration soll $<0.1M$ und die Konzentration von Al, Cr oder Fe soll $<0.05M$ sein.

2. Eine spezielle Methode wird vorgeschlagen, welche die Bestimmung erlaubt von 1-2 mg Hg in 20 ml Lösung, welche einen grossen Überschuss von Wismuth ($\gtrsim$ 98%) enthält in Gegenwart von Ethylendiamintetraacetat. Fehler 0-3%.

3. Eine Methode wird angegeben, die ermöglicht Quecksilber neben einem Überschuss von Kupfer in essigsaurer Lösung von Ethylendiamintetraacetat zu bestimmen.

4. Eine spezielle Methode wird vorgeschlagen, die es ermöglicht 1-2 mg Quecksilber in 30 ml Lösung, welche einen grossen Überschuss von Kupfer (>98%) enthält, zu bestimmen. Die Titration wird in alkalischer Lösung von Na_3-Citrat ausgeführt. Die Titration verläuft rasch. Fehler 0-2%.

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URANYL-ALIZARIN RED-S COMPLEX. A SPECTROPHOTOMETRIC STUDY

by

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DE BOER[1] noted that uranyl salts produce a violet colouration with alizarin red-S. Recently the intense red colour, produced upon addition of alizarin red-S to a tetravalent uranium solution has been used for colorimetric estimation of traces of uranium[2]. The wave length of maximum absorption of this complex is 525 mμ, which coincides almost with that given by tetravalent elements like Th, Zr, *etc.* In this communication detailed studies on the nature of the uranyl-alizarin red-S complex together with the effects of pH on the complex are reported. This violet coloured complex with its absorption peak at 570 mμ is formed in neutral or slightly alkaline solutions. Structurally, as judged from absorption spectra, two types of metal complexes with alizarin red-S seem to exist. In one class the absorption maximum is at about 520 mμ while in others it shifts to about 570 mμ. Zr, Hf, Th, *etc.*[3] belong to the first group and uranyl to the second group. A factor in the understanding of the structures of the complexes from absorption spectra is the change in absorption of the dye with pH.

EXPERIMENTAL

Reagents: — (1) *Uranyl solution:* — A stock solution of pure uranyl nitrate was prepared as described earlier[4]. It was suitably diluted to give a solution of 0.9995 $\cdot 10^{-3} M$ in double-distilled water.

(2) Alizarin red-S solution has been prepared by dissolving 0.1701 g of a Merck sample in 500 ml of double-distilled water. This gave a solution 0.9945 $\cdot 10^{-3} M$.

(3) pH adjustments were made by adding requisite amounts of freshly distilled and diluted ammonia or dilute acetic acid on a bench type Cambridge pH-meter using a glass electrode.

Absorption measurements were made with a Beckman D.U. model spectrophotometer in 1 cm matched glass cuvettes. The source of light was a hot filament tungsten lamp. The slit was about 0.02 mm on the scale giving a band width of 0.6 mμ at the less refrangible end.

Fig. 1. shows the transmission characteristics of the reagent, and of the uranyl complex at a pH of about 8.2. It is seen from the curves that the reagent has

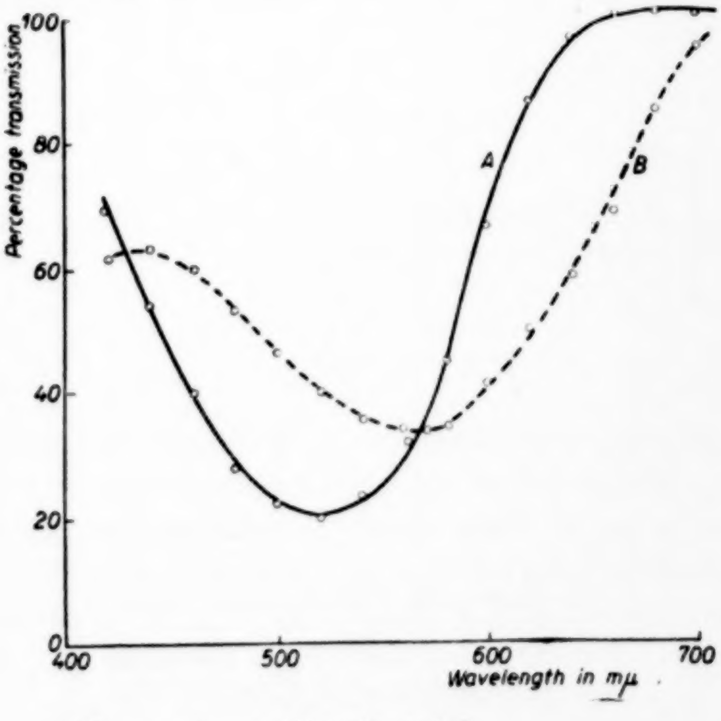


Fig. 1. A — Alizarin red-S
B — Uranyl complex of the dye

a transmission minimum at 520 mμ while that of the complex appears at 570 mμ. The maximum difference in density between the reagent and the complex lies however at 620 mμ.

Determination of optimum pH for the complex

The reagent shows no significant changes in absorption in the pH region[4-10]. The absorption of the complex in its dependence upon pH was studied as follows. 10 ml of uranyl nitrate and 10 ml of the reagent were mixed and adjusted to the desired pH by adding dilute ammonia. The solution was then diluted to 100 ml with water of identical pH. The absorptions are given in Table I.

TABLE I

Wave length *mμ*	*Reagent*	*Transmission of the complex at pH*			
		5.21	*6.8*	*8.12*	*8.62*
580	69.2	68.5	64.5	60.0	61.3
560	56.9	66.6	62.5	59.0	59.5
540	48.1	67.0	62.9	59.0	60.0
520	44.8	71.0	65.6	63.1	62.4

One significant effect of complexation is the decrease in absorption at 520 mμ, with a rise at 580 mμ. While there is evidence of partial complexation even at pH 5.2, the process does not appear to be complete till a pH of 8.1 is reached; further rise in pH gives rise to no significant change in absorption. A pH of 8.3 was thus selected for further studies.

Composition of the complex. The composition of the complex was studied by three different optical methods, *viz.* (a) JOB's method of continuous variations[5], (b) Molar ratio[6] and (c) Slope ratio[7] methods. A modification of the slope ratio method which has been found more convenient in this laboratory is shown in Fig. 3. In this, instead of plotting the intensities versus the analytical concentration of the variable component

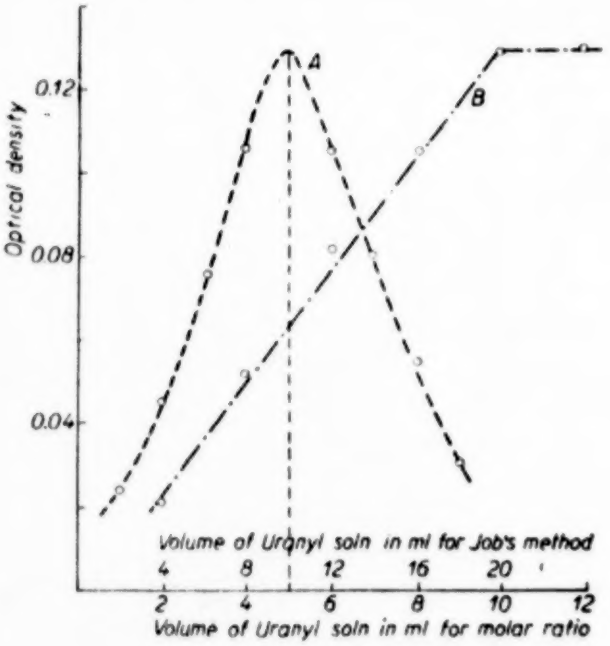


Fig. 2. At 620 mμ: (A) JOB's method; (B) Molar ratio method

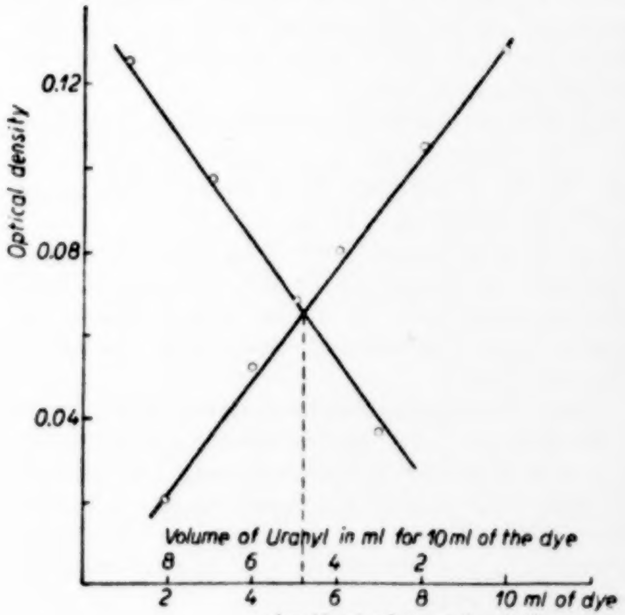


Fig. 3. Modification of slope ratio method (at 620 mμ)

from the same origin, the two plots stem from two origins at either end of the X-axis, the interval of separation being equal to the concentration of the excess component, which should be the same. While all the methods point to a 1:1 ratio of the uranyl and the dye, some interesting conclusions may be drawn from the appearance of the curves in JOB's procedure and molar ratio method, Fig. 2. The former shows a sharp peak which indicates high stability for the complex while the sharp turn in the molar ratio curve goes to confirm this conclusion. Further evidence of insignificant dissociation of the complex was obtained as follows. Varying amounts of uranyl solution were mixed with equal amounts of the dye of the same molarity and diluted always to the same standard volume. Thus the concentration of the complex varied 8-fold in the following series of experiments.

(1) 2.5 ml of uranyl solution and 2.5 ml of dye diluted to 100 ml
(2) 5.0 ml ,, ,, ,, ,, 5.0 ml ,, ,, ,, ,, 100 ,,
(3) 10.0 ml ,, ,, ,, ,, 10.0 ml ,, ,, ,, ,, 100 ,,
(4) 15.0 ml ,, ,, ,, ,, 15.0 ml ,, ,, ,, ,, 100 ,,
(5) 20.0 ml ,, ,, ,, ,, 20.0 ml ,, ,, ,, ,, 100 ,,

When the absorption are plotted against the theoretical concentrations of the complex at two different wavelengths 560 and 620 mμ straight lines resulted, Fig. 4.

Structure of uranyl-alizarin complex. At the pH of formation of the complex, the absorption peak of alizarin red-S lies at 520 mμ which on complexation with uranyl shifts to 570 mμ. DORTA-SCHAEPPI *et al.*[8] made an attempt to explain the absorption of alizarin in neutral and alkaline solutions as well as on complexation with fourth group elements on the free electron-model developed by KUHN[9]. The results obtained do not appear to be quite convincing. According to KUHN, the peak of first absorption is determined by the number of 'free' electrons and the length of the electron path. A clearer rendering of the terms 'free' electrons, and 'length of the vibrating chain', has been given by RÜDENBERG AND SCHERR[10]. The number of free electrons may be deduced from those in excess to form a skeleton structure of the molecule in which the atoms are all presumed to be bound by single valence bonds. The length of the chain is assumed to be the sum of the individual bond distances plus a bond length at each free end. KUHN developed his theory to the case of chains containing conjugated C-C bonds with N at each end, and RÜDENBERG AND SCHERR only to the C-C chains. The C-C distance has been assumed from data on aromatic compounds as 1.39 A and KUHN appropriated the same value for the C-N bond which does not however appreciably differ from the former. In a molecule of alizarin type, it appears reasonable to employ other values for the >C=O or →C-O bonds; and in the computation of the bond length beyond

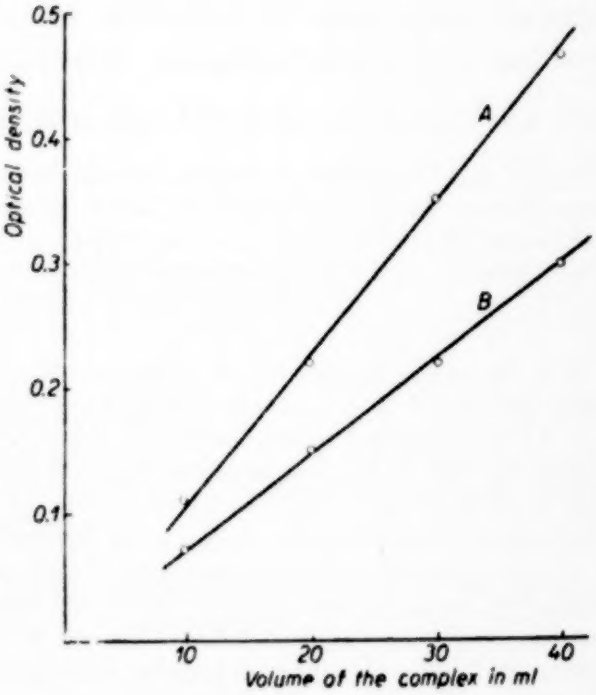
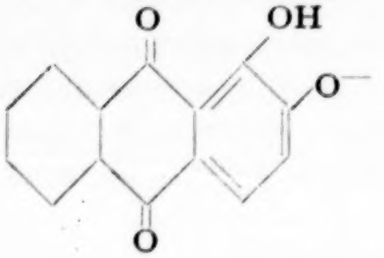


Fig. 4. A — At 560 mμ
B — At 620 mμ

the free end, the immediately preceeding bonds should also be taken into consideration.

Different structures have to be postulated for the alizarin molecule in its uncombined stage in acid, neutral and alkaline solutions. In the pH range 4—10 corresponding to a neutral solution, the β-hydroxyl ionizes and the alizarin anion resonates between the two structures.



The resonating chain may be represented as

$$HO{-}C{=}C{-}C{=}C{-}C{=}C{-}O^{-}$$

with C-C distances equal to 1.39 A, and C-O, 1.36 and O-H as 0.96 A. Substitution in KUHN's equation

$$\lambda = \frac{8\,mc}{h} \cdot \frac{L^2}{N+1}$$

where $L = 11.99$ and $N = 8$ gives for λ the value 527 mμ which compares very favourably with the observed position at 520 mμ.

On complexation with uranyl, the chain is lengthened on account of the greater ionic volume of UO_2. It is known that U-O distance is of the order of 1.9 A[11] and if this value were adopted in place of C-O length of 1.36, beyond the free end-point, the absorption peak would shift to 585 mμ. The U-O distance employed is that of the covalent bond and this is modified by the partial ionic character of the bond; the absorption peak may be expected to lie at a shorter wave length. The experimental position of 570 mμ compares very favourably with expectation.

SUMMARY

From spectrochemical studies on the blue complex resulting from uranyl and alizarin-S, it has been shown that a compound in the stoichiometric ratio 1:1 of uranyl and reagent is formed. The compound is stable at pH 8.2. The peaks of absorption of the reagent at 520 mμ and of the uranyl compound at 570 mμ have been accounted for, applying KUHN's relationship.

RÉSUMÉ

A la suite des études sur le complexe bleu résultant de la réaction uranyle et alizarine-S, il a été démontré qu'il se forme un composé de l'uranyle et du réactif, dans le rapport stoechiométrique 1:1. Le composé est stable au pH 8.2. Les absorptions maximums du réactif à 520 mμ et du composé à 570 mμ ont été expliquées au moyen de la relation de KUHN.

ZUSAMMENFASSUNG

An Hand von spektrochemischen Untersuchungen des von Uranyl und Alizarin-S entstehenden blauen Komplexes wird gezeigt, dass sich eine Verbindung im stöchiometrischen Verhältnis 1:1 von Uranyl und dem Reagenz bildet. Bei pH 8.2. ist die Verbindung stabil. Die Absorptionsspitzen des Reagenzes bei 520 mμ und die der Uranylverbindung bei 570 mμ werden erklärt, indem man die KUHNsche Relation anwendet.

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ÉTUDE COMPARÉE DE QUELQUES MÉTHODES DE DOSAGE DE L'ACIDE SALICYLIQUE DANS LE SÉRUM SANGUIN

par

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Ce travail, entrepris en collaboration avec M. le Prof. E. MARTIN, directeur de la Policlinique médicale universitaire de Genève, a été effectué à propos d'une série d'essais cliniques sur un nouveau médicament*. Les résultats des essais cliniques ont été publiés d'autre part dans „Praxis".

Les méthodes étudiées sont les suivantes:

Méthodes par précipitation:

a) méthode du Dr. BENGER — utilisée à Vienne par MICZOCH ET TREMI[1] au cours d'un travail analogue;

b) méthode du Dr. BENGER modifiée.

Méthode par extraction:

c) méthode de SMITH et coll.[2] adaptée à la spectrophotométrie.

I. MÉTHODE DU DR. BENGER

Cette méthode est une adaptation de celle d'OROCZO ET GUERRA[3]: au sérum, déprotéinisé par le tungstate de sodium et l'acide sulfurique, on ajoute une solution de fer(III), de manière à former le complexe violet avec l'acide salicylique. La coloration, proportionnelle à la concentration de l'acide salicylique, est déterminée par colorimétrie. Les protéines retenant une partie de l'acide salicylique par adsorption[4,5], les courbes d'étalonnage doivent être établies au moyen de sérum pur additionné *in vitro* de quantités variables d'acide salicylique.

1. *Description de la méthode* (préparation des étalons)

A 1 ml de sérum non hémolysé on ajoute X ml d'une solution $2.10^{-3}M$ d'acide salicylique, $(7-X)$ ml d'eau, 1 ml de $Na_2WO_4.2H_2O$ à 10 %, 1 ml d'acide sulfurique $2/3N$. On agite, filtre, prélève 5 ml du filtrat auxquels on ajoute encore 0.3 ml d'une solution de nitrate de fer(III) (à 0.1 % en fer). On agite et on effectue rapidement la colorimétrie — un trouble empêchant les mesures apparaît après quelques minutes.

Dans le cas des dosages, on remplace la solution d'acide salicylique par de l'eau: 7 ml au total.

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* Il s'agit de l'Iromine, acétylsalicylate de calcium dont l'eau de cristallisation a été remplacée par une molécule d'urée. Ce médicament est fabriqué par Darmosan S.A., St. Gall.

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2. *Conditions expérimentales*

Réactifs: Merck, puriss. pro analysis. Colorimètre:Spekker-Hilger, filtre No. 604.

Sérum: mélange de sérums provenant d'une dizaine de malades n'ayant pas subi de traitement récent.

Témoin: les mesures sont effectuées par rapport à une solution préparée selon la technique décrite à partir du sérum pur.

3. *Résultats des essais*

a) Le trouble empêche les mesures dans presque le 50 % des cas — il semble que sa formation est accélérée au cours même de la mesure, sous l'influence du flux lumineux assez intense de notre appareil. Dans les cas limites, on ne remarque qu'un effet Tyndall plus ou moins net.

b) Les densités optiques des solutions limpides ne sont en général pas reproductibles.

c) Elles deviennent sensiblement reproductibles lorsqu'on travaille parallèlement et simultanément sur plusieurs échantillons.

Ainsi la Fig. 1 montre quatre courbes d'étalonnage, établies l'une après l'autre, mais où tous les points d'une même courbe ont été déterminés sur des échantillons traités simultanément.

d) Des solutions d'acide salicylique dans l'eau, de concentrations correspondantes à celles dans le sérum, et sur lesquelles sont effectuées les opérations décrites plus haut, ne donnent pratiquement aucune coloration. Le trouble est d'ailleurs exceptionnellement abondant.

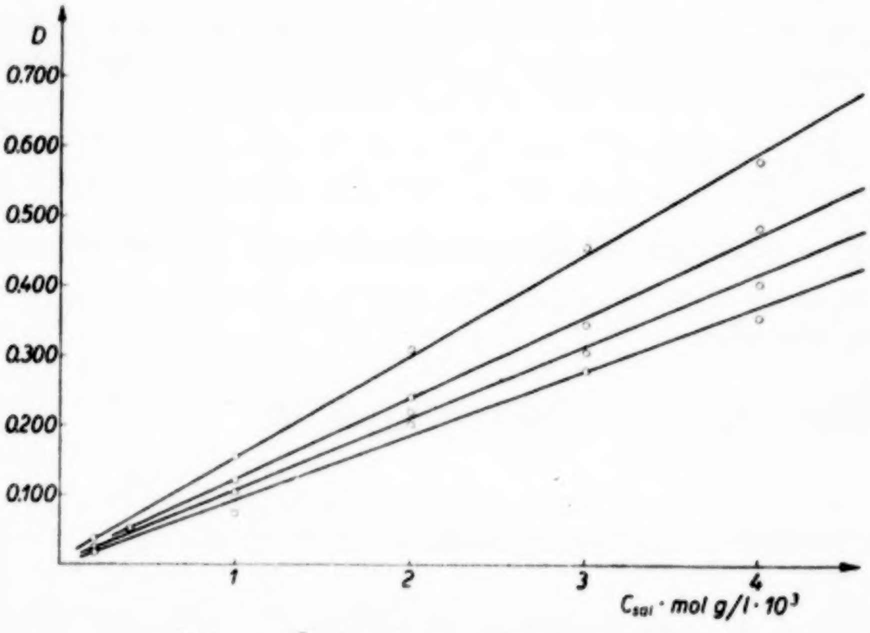

Fig. 1. Étude de la reproductibilité.

4. *Discussion des résultats*

Le point d) ci-dessus montre que les variations de coloration, mises en évidence par la Fig. 1 ne proviennent pas uniquement de la variation de la rétention de l'acide salicylique par les protéines, due aux petits écarts de manipulations. Le tungstate de sodium et l'acide sulfurique jouent certainement un rôle prépondérant, ainsi que le pH qui pourrait être fixé par un tampon.

Deux processus sont susceptibles de diminuer la coloration:

a) le tungstate peut former avec l'acide salicylique un complexe de formule $NaWO_2(OH)C_6H_4OCO_2$, plus ou moins soluble suivant le pH[6,7].

b) le tungstate peut se décomposer sous l'influence d'un acide minéral (H_2SO_4) en paratungstate (de formule généralement admise $12\ WO_3.5Na_2O$) qui donne avec les sels ferriques des substances cristallines peu solubles se comportant comme des complexes[6,8,9,10].

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Il est possible qu'en effectuant les mesures sur un autre type de colorimètre — ayant un effet thermique ou photochimique moins marqué — le trouble soit moins gênant. Même si celà était le cas, la méthode ne serait pas recommandable. Elle est inapplicable dans nos conditions de travail.

II. MÉTHODE DU DR. BENGER MODIFIÉE

La méthode précédente peut être améliorée en fixant le pH par un tampon, et en éliminant l'influence du tungstate.

1. Choix d'une solution tampon

Les équilibres qui régissent la formation du complexe coloré (RFe^{+2}) sont schématiquement les suivants, si RH représente l'acide salicylique:

$$RH \rightleftarrows R^- + H^+ \qquad (1)$$

$$Fe^{+3} + R^- \rightleftarrows RFe^{+2} \qquad (2)$$

$$Fe^{+3} + 3\,OH^- \rightleftarrows Fe(OH)_3 \qquad (3)$$

$$H_2O \rightleftarrows H^+ + OH^- \qquad (4)$$

La concentration de RFe^{+2} sera d'autant plus grande que les concentrations de R^- et de Fe^{+3} seront elles-mêmes plus grandes (équilibre déplacé vers la droite dans la réaction (2). Ceci implique pour la réaction (1) que le pH devra être aussi alcalin que possible, alors que pour les réactions (3) et (4) il devra être aussi acide que possible. En pratique il suffira de se trouver à un pH un peu inférieur au pH de début de précipitation de l'hydroxyde ferrique: le pH 2.5 convient parfaitement.

Les tampons usuels de pH 2.5 sont inutilisables car ils perturbent la réaction (précipitation avec le fer par exemple). Le tampon monochloracétique est satisfaisant à condition de ne pas être chauffé en présence de fer. Le p*K* de l'acide monochloracétique étant de 2.9, l'effet tampon est encore très bon à pH 2.5.

Préparation du tampon: 4.725 g d'acide monochloracétique (1 mol/10, soit la quantité nécessaire pour préparer 500 ml de tampon *M*/10) sont amenés à pH 2.5 par NaOH *N*/10. La neutralisation est effectuée au pH mètre Beckman de manière à ce que le volume final soit de 500 ml.

2. Elimination de l'influence du tungstate

Les substances qui pourraient complexer l'excès de tungstate gênent par ailleurs la réaction. On peut toutefois ajouter un excès de fer suffisant pour fixer tout le tungstate et déplacer en même temps l'équilibre de la réaction (2) de manière à ce que de petites variations de la concentration finale du fer restent négligeables.

La filtration du trouble étant extrêmement difficile, même après chauffage, l'addition du fer doit précéder la déprotéinisation: le précipité de protéines agit ainsi comme aide filtrant.

Pour les quantités de sérum et de déprotéinisants utilisés dans la méthode BENGER, 1 ml d'une solution d'alun ferrique, à 0.5 % en fer, suffit à éliminer le tungstate. La solution reste parfaitement limpide après 24 heures. Une variation de volume de la solution ferrique de ± 0.1 ml (soit ± 10 %) n'entraîne pas une variation de la densité optique supérieure à 3 %. En pratique les variations de la concentration du fer étant bien inférieures à 10 %, la précision est suffisante. Par mesure de sécurité, on peut toutefois ajouter encore 0.2 ml de la solution ferrique en même temps que le tampon, au moment de la mesure.

3. *Description de la méthode*

Introduire dans des éprouvettes 1 ml de sérum non hémolysé, (5-X) ml d'eau distillée, X ml d'une solution $2 \cdot 10^{-3} M$ d'acide salicylique, 1 ml d'une solution de tungstate de sodium à 10 %, 1 ml d'acide sulfurique $2/3 N$ (agiter fortement), enfin 1 ml de la solution d'alun ferrique à 0.5 % en fer. Agiter fortement. Les éprouvettes sont chauffées 15 minutes exactement dans un bécher d'un litre contenant 400 ml d'eau, maintenue juste au-dessous de l'ébullition par une plaque chauffante électrique.

Refroidir dans de l'eau froide, filtrer une ou deux fois, contrôler la limpidité contre une forte lampe et faire des prises de 5 ml dans chaque éprouvette. Ajouter à ces prises 2 ml de tampon 2.5 et 0.2 ml de solution ferrique. Effectuer les mesures dans des cuves de 1 cm, sur le colorimètre muni d'un filtre No. 604.

Pour les dosages on remplace la solution d'acide salicylique par de l'eau distillée.

4. *Valeur de la méthode*

La Fig. 2 donne une courbe d'étalonnage typique.

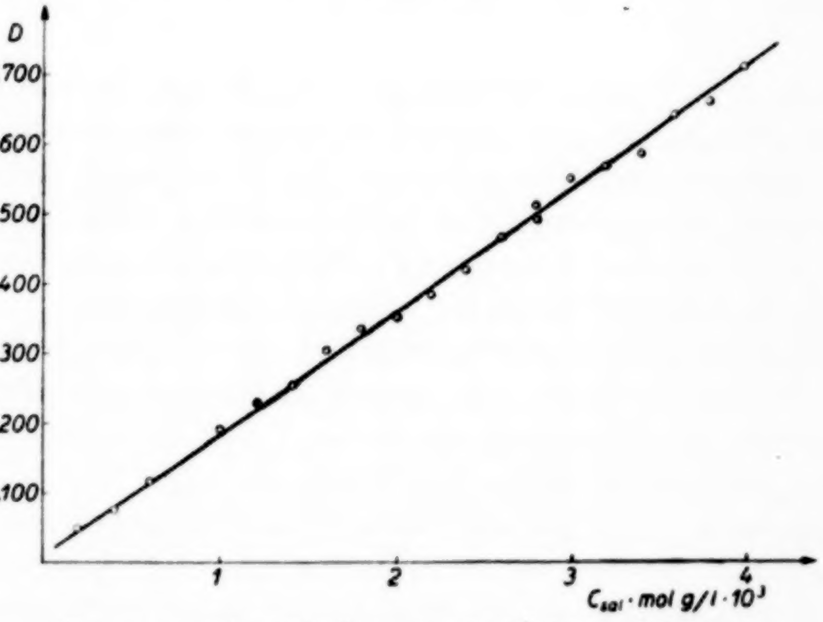

Fig. 2. Courbe d'étalonnage de l'acide salicylique.

Les valeurs de la salicylémie s'obtiennent en mg % en multipliant X par 27.6, et en g/l en multipliant X par 0.276.

Un calcul d'erreur donne les résultats suivants pour la précision de la méthode, en fonction de l'ordre de grandeur de X:

Valeur de X	*Salicylémie* mg %	*Erreur max.* ± mg %	*Erreur max.* ± %
0.2	5.5	1.0	18
1.0	27.6	1.3	4.7
2.0	55.2	1.4	2.6

Cette précision est suffisante pour un dosage biologique, les quantités maximum à doser étant de l'ordre de 50 mg %. La méthode demande cependant une assez longue

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adaptation de l'opérateur qui doit arriver à maîtriser parfaitement les facteurs personnels variables d'un essai à l'autre. Elle n'est pas recommandable pour un laboratoire où elle ne pourrait pas être appliquée dans le plus grand calme.

III. MÉTHODE PAR EXTRACTION

La méthode **Benger** modifiée ne présente plus les avantages de simplicité et de rapidité qu'on attend d'une méthode par précipitation, lorsqu'on la préfère à une méthode par extraction généralement plus précise.

Si elle a permis, au début des essais cliniques, d'effectuer à notre satisfaction toute une série de dosages, nous lui avons finalement préféré une méthode par extraction, selon **Smith** et coll.[2]. Initialement décrite comme méthode colorimétrique, la méthode gagne à être adaptée à la spectrophotométrie. Certains écarts liés à une hémolyse partielle du sérum sont en effet éliminés lorsqu'on travaille en lumière monochromatique.

1. *Solutions nécessaires*

Les réactifs sont de pureté "puriss, pro analysis".

Solution A: 0.5 g d'acide salicylique + 3.5 ml de NaOH *N* amené à 100 ml. Etalon primaire à 5 mg/ml conservé à la chambre froide.

Solution B: 10 ml de sol.A amenés à 100 ml. Etalon secondaire à 0.5 mg/ml.

Solutions étalons:

a) 5 ml de sol. B amenés à 25 ml = 0.1 mg/ml = 10 mg%.
b) 10 ml ,, ,, ,, ,, ,, 25 ,, = 0.2 ,, = 20 ,,
c) 15 ml ,, ,, ,, ,, ,, 25 ,, = 0.3 ,, = 30 ,,
d) 20 ml ,, ,, ,, ,, ,, 25 ,, = 0.4 ,, = 40 ,,
e) 25 ml de solution B = 0.5 ,, = 50 ,,

Solution C: 0.25 g de $Fe(NO_3)_3 \cdot 9H_2O$ + 0.12 ml HNO_3 ($d = 1.4$) amenés à 1 litre (HNO_3 $1.75 \cdot 10^{-4} N$).

Solution D: HCl 5*N*.

Dichloréthylène.

2. *Description de la méthode*

Introduire 1 ml de sérum dans un flacon rôdé de 50 ml, ajouter 1 ml de solution étalon, 0.5 ml de sol.D et 25 ml de dichloréthylène. Agiter vigoureusement pendant 5 minutes, puis centrifuger 5 minutes à vitesse moyenne. Les protéines forment un gâteau compact à l'interface des deux liquides, surmonté de la solution aqueuse qui est aspirée à la trompe au moyen d'une pipette capillaire.

En inclinant le tube, le gâteau se détache des parois. Ceci permet de faire une prise de 20 ml de la solution de dichloréthylène, qui est transvasée dans un nouveau flacon rôdé de 50 ml et agitée vigoureusement pendant 5 minutes avec 10 ml de solution C. Après nouvelle centrifugation on fait une prise de la solution aqueuse dont on détermine la densité optique à 530 mμ, sur un spectrophotomètre Unicam.

Lors des dosages la solution étalon est remplacée par 1 ml d'eau distillée.

3. *Valeur de la méthode et conclusion*

La méthode par extraction est plus fidèle que la méthode **Benger** modifiée. Elle ne nécessite pas une aussi grande rigueur dans les manipulations, évite les filtrations délicates et ne demande pratiquement pas plus de temps que cette dernière.

Le calcul d'erreur montre la reproductibilité des densités optiques en fonction de la teneur en salicylate:

Salicylémie mg %	*Densité optique D*	*Erreur max. sur D(±)*	*Erreur max. % (±)*
10	0.070	0.003	4.3
20	0.140	0.005	3.6
30	0.210	0.007	3.4
40	0.280	0.012	2.4
50	0.350	0.016	2.2

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Dans la région de concentrations intéressante, l'erreur est donc inférieure à celle de la méthode BENGER modifiée.

Nous estimons en conséquence que la méthode par extraction doit être préférée aux autres méthodes étudiées. Parmi celles-ci, la méthode BENGER n'offre pas d'intérêt alors que la méthode modifiée peut, sous certaines réserves, conduire à des résultats satisfaisants.

RÉSUMÉ

Lorsqu'on déprotéinise le sérum sanguin par le tungstate de sodium et l'acide sulfurique, l'excès de tungstate gêne la formation du complexe coloré de l'acide salicylique avec le fer. Les réactions qui interviennent sont encore assez mal connues. On peut toutefois utiliser la méthode si la concentration du fer répond à certaines conditions — excès suffisant pour éliminer tout le tungstate. La méthode devient alors lente et délicate. On montre finalement que la méthode la plus satisfaisante consiste à extraire l'acide salicylique par le dichloréthylène, puis à le faire repasser en phase aqueuse au moyen d'une solution ferrique.

SUMMARY

If one deproteinises blood serum by sodium tungstate and sulphuric acid, the excess tungstate impedes the formation of the colourless complex of salicylic acid with the iron. The intervening reactions are not yet well understood. One can use this method if a sufficient concentration of iron is present to eliminate all the tungstate; but the method then becomes slow and delicate. It is shown finally that the most satisfactory method consists of extracting the salicylic acid by dichlorethylene and then bringing it again into aqueous solution by means of a ferric solution.

ZUSAMMENFASSUNG

Wenn man das Blutserum mit Natriumwolframat und Schwefelsäure enteiweisst, stört der Überschuss von Wolframat die Bildung des gefärbten Komplexes der Salizylsäure mit dem Eisen. Die entsprechenden Reaktionen sind noch wenig bekannt. Man kann aber trotzdem diese Methode verwenden, wenn die Eisenkonzentration gewissen Bedingungen entspricht ein genügender Überschuss um alles Wolframat auszuscheiden. Die Methode wird so lang und delikat. Man zeigt schliesslich, dass die am besten befriedigende Methode darin besteht, die Salizylsäure mit Dichlorethylen auszuziehen, dann sie wieder in eine wässrige Phase zu bringen mit Hilfe einer Eisen (III)-Lösung.

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DOSAGE DE L'HISTIDINE
I. ÉTUDE POLAROGRAPHIQUE ET DOSAGE DU DINITROFLUOROBENZÈNE

par

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INTRODUCTION

L'histidine peut être séparée des hydrolysats protéiques des matières organiques comme sel d'argent[1], comme complexe mercurique[2], comme diflavianate[3] ou mieux encore comme nitranilate[4]. Ces méthodes ont été modifiées et améliorées par plusieurs chercheurs[5-12].

La précipitation de l'histidine comme sel d'argent est quantitative. L'acide nitranilique permet une séparation quantitative de petites quantités de cet acide aminé.

L'histidine réagit avec l'acide *p*-diazobenzène-sulfonique (ou autres acides semblables comme l'acide *p*-diazobenzène-arsonique), en milieu alcalin, en donnant une coloration rouge[13]. Ce fait a permis l'établissement d'un dosage colorimétrique qui a fait l'objet de nombreuses études[14,15,16]. La sensibilité de la méthode est de 1:100.000. La quantité minimum qui peut être dosée est de 0.01 mg d'histidine[17,18]. Ce procédé n'est pas spécifique. Le réactif réagissant aussi avec la tyrosine, les phénols, la guanine, l'adénine, les imidazoles, les sulfures, les ions ammonium, *etc.* De plus, l'intensité de la coloration est fortement influencée par les conditions de la réaction[14]. En séparant l'histidine de la tyrosine par microchromatographie, on arrive néanmoins à doser par cette méthode de 0.004 à 0.025 mg d'histidine[19].

En copulant l'histidine avec la *p*-bromoaniline, il se produit une couleur rouge qui permet une colorimétrie de petites quantités de cet acide aminé (jusqu'à 0.0026 mg)[20]. Cette méthode a été modifée par l'emploi de la *p*-anisidine diazotée[21,22].

En traitant l'histidine, ou ses sels, avec léger excès d'eau de brome à chaud, la solution se colore en rouge intense. En se basant sur cette réaction, on peut doser jusqu'à 0.15 mg d'histidine[23-34].

La séparation des acides aminés par chromatographie sur colonne ou sur papier est bien connue. Après séparation chromatographique sur papier, on révèle généralement les spots des acides aminés avec l'hydrate de tricétohydrindène (ninhydrine). Les spots ainsi colorés sont élués et le dosage achevé par colorimétrie.

Une autre méthode de séparation chromatographique des acides aminés est celle basée sur la formation du N-2, 4-dinitrophényl-acide aminé à partir du 1-fluoro-2,4-dinitrobenzène[35-41]. Il n'est pas nécessaire ici de révéler les spots, ces dérivés étant colorés.

Nous nous sommes proposés, de mettre au point un dosage polarographique de l'histidine par formation du di-N-dinitrophényl-histidine en se basant sur le dosage polarographique des dérivés nitrés des acides aminés et autres composés organiques, faits dans ces laboratoires[42,43,44].

Dans ce but, nous avons d'abord effectué l'étude et le dosage polarographique du 1-fluoro-2, 4-dinitrobenzène (DNFB.) ce qui fait l'objet de la première partie de ce travail, puis nous avons mis au point le dosage de l'histidine après avoir examiné le comportement polarographique de la di-DNP-histidine(di-DNP).

ÉTUDE ET DOSAGE POLAROGRAPHIQUE DU 1-FLUORO-2,4-DINITROBENZÈNE (DNFB)

I. GÉNÉRALITÉS

Le 1-fluoro-2,4-dinitrobenzène utilisé par SANGER[36] dans son étude de l'insuline a été repris par lui et par d'autres chercheurs[37-41] comme réactif quantitatif des fonctions amino libres.

Ce réactif attaque énergiquement la fonction amino libre pour former un dérivé N-dinitrophenyl. Lorsqu'il s'agit de protéines ou de peptides, le DNFB attaque seulement les fonctions amino libres terminales. La liaison N-DNP est stable, elle résiste à l'hydrolyse acide. Remarquons encore que bien que le fluor, dans les composés aliphatiques à liaisons C-F, soit moins réactif que le chlore dans les composés chlorés correspondants, l'atome de fluor, dans le DNFB est plus actif que l'atome de chlore dans le DNCB[36-45].

Le DNFB est relativement peu toxique, mais possède une action vésicante. Le corps pur est un liquide incolore qui jaunit avec le temps. P.E.: 136-138° sous 2 mm/Hg[45] et 149-154° sous 3 mm/Hg[40].

Nous avons tout d'abord effectué une étude polarographique de ce réactif, en vue de son dosage.

Nous avons utilisé un DNFB de la Maison „Hoffmann-La Roche".

II. PARTIE EXPERIMENTALE

On sait que l'ion hydrogène intervient dans la réduction polarographique des dérivés nitrés. C'est pourquoi l'étude du DNFB a été faite en présence de tampons dont la constitution est donnée dans le Tableau I.

TABLEAU I

pH	*Acide critique 0.1M*	*Phosphate disodique 0.2M*
2.2	19.60 ml	0.40 ml
3	15.89	4.11
4	12.29	7.71
5	9.70	10.30
7	3.53	16.47
8	0.55	19.45
9.24	Borax 1/20*M*	—
10	Carbonate de sodium 0.2*M*	Carbonate acide de sodium 0.1*M*

Tous ces tampons ont été préparés avec des produits „Merck" pro anal. Les pH ont été vérifiés au pH-mètre „Beckman".

La gélatine n'a pas pu être employée pour supprimer les maximums des courbes polarographiques, le DNFB réagissant avec les fonctions amino-libres présentes dans celle-ci. Pour la même raison, on ne peut utiliser un corps possédant une fonction sulfhydrile[36]. Nous avons trouvé, par contre, que l'alcool polyvinylique (de la Maison „Lonza-Bâle" — Type K 44/100) donnait de bons résultats.

Le DNFB n'étant pas soluble dans l'eau, nous l'avons solubilisé dans l'alcool absolu.

Etude systématique en fonction du pH

Préparation des solutions

186.1 mg de DNFB sont dissous dans 100 ml d'alcool absolu. 10 ml de cette solution sont versés dans un ballon jaugé de 100 ml, au moyen d'une microburette. On ajoute alors 10 ml d'alcool absolu, 50 ml de tampon (voir Tableau I) et on complète le volume avec de l'eau bidistillée. Nous obtenons donc une solution de DNFB $10^{-3}M$ d'une teneur en alcool de 20%.

Une première étude a été effectuée sur cinq solutions ainsi préparées et contenant les tampons de pH 3 à 8. Pour supprimer les maximums nous avons utilisé une solution d'alcool polyvinylique à 2% dans l'eau bidistillée. Une goutte de cette dernière est suffisante.

Remarque: Dans tout notre travail, nous avons, avant chaque polarogramme, chassé l'oxygène de nos solutions en y faisant barboter de l'hydrogène pendant dix minutes.

Pour cette étude, nous avons utilisé le Polarographe „Sargent XXI". Les résultats figurent dans le Tableau II, les potentiels de demi-sauts ($E_{1/2}$) sont mesurés par rapport à la surface de mercure prise comme anode, et sont tous de signe négatif.

TABLEAU II

CONCENTRATION DE DNFB $10^{-3}M$

pH	i_1 (*μA*)	i_2 (*μA*)	i_3 (*μA*)	i_{tot} (*μA*)	i_1/i_2	$E^1{}_{1/2}$ *volt*	$E^2{}_{1/2}$ *volt*	$E^3{}_{1/2}$ *volt*	i_1/k	i_2/k	i_3/k	i_{tot}/k
2.2	12.9	14.4	—	27.3	0.9	0.51	0.82	—	5.45	6.08	—	11.53
3	13.8	10.95	—	24.75	1.26	0.53	0.82	—	5.82	4.62	—	10.24
4	14.7	11.4	—	26.1	1.30	0.56	0.86	—	6.20	4.80	—	10.00
5	15	11.7	—	26.7	1.29	0.62	0.92	—	6.35	4.94	—	11.29
7	14.4	11.2	—	25.6	1.29	0.64	0.92	—	6.18	4.73	—	10,81
8	10.5	3.9	9.6	24.0	2.70	0.69	0.94	1.30	5.45	1.67	4.12	10.30
9.24	10.2	8.6	4.6	23.4	1.19	0.73	0.93	1.34	4.38	3.68	1.97	10.—
10	7.2	6.0	11.4	24.6	1.20	0.70	0.89	1.18	3.09	2.57	4.90	10.55

D'autre part le courant de diffusion est aussi égal selon Ilkovic à:

$i_d = 605 \cdot n \cdot D^{1/2} \cdot m^{2/3} \cdot t^{1/6} \cdot c$.

Appelons k le produit: $m^{2/3} \cdot t^{1/6} \cdot c$

ou:

m = masse de mercure en mg/sec
t = temps de goutte en sec
c = concentration de DNFB en millimol/litre.

Le temps de chute d'une goutte de mercure étant de 2.94 sec et la masse de mercure égale à 2.72 mg/sec (hauteur de la colonne de mercure: 17 cm) nous trouvons $k = 2.335$, pour $c = 1$.

On observe aux pH acide et neutre, la présence de deux sauts lors de la réduction polarographique du DNFB. Aux pH 3, 4, 5 et 7, le premier saut est plus grand que le second dans un rapport de 5/4. Au pH 2.2 le rapport i_1/i_2 est de 6/5. Au pH 8, nous remarquons l'apparition d'un troisième saut qui subsiste aux pH 9.24 et 10.

Le i_d total de ces trois sauts est sensiblement égal à celui des deux sauts observés à pH acide et neutre. $i_{tot/k}$ est à peu près constant pour tous les pH. Nous en déduisons que dans la réduction globale du DNFB du pH 3 au pH 10, intervient le même nombre d'électrons, dont la détermination sera exposée plus loin. Il est possible que le troisième saut aux pH 8, 9.24 et 10 soit dû à la formation du dinitrophénétole.

La variation de $E_{1/2}$ en fonction du pH montre que l'ion hydrogène intervient dans la réaction de réduction sur la goutte de mercure. Nous avons choisi pour l'établissement de la courbe d'étalonnage les pH 5 et 10.

III. ESSAIS DE LA STABILITÉ AU pH 5

Des solutions contenant 2 mg de DNFB dans 10 ml 50% de solution tampon de pH 5, 20% d'alcool absolu et 4 gouttes d'une solution d'alcool polyvinylique à 0.2% ont été polarographiées en fonction du temps. Les essais ont été effectués après 15, 30, 60 minutes, 2, 8, 24 et 48 heures. Les polarogrammes sont parfaitement reproductibles. Les $E_{1/2}$ et les hauteurs des sauts ne varient en aucun cas pendant cette période.

D'autre part, nous avons remarqué qu'une solution de DNFB fraîchement préparée est pratiquement incolore, mais après sept ou huit heures, elle se colore en jaune. La hauteur des sauts obtenus à partir de ces solutions colorées ou non, ne varie pas. On peut en conclure que la coloration n'influence pas les polarogrammes.

IV. SOLUBILITÉ ET STABILITÉ AU pH 10

Nous avons trouvé que le DNFB est quelque peu soluble dans une solution aqueuse contenant uniquement 50% de tampon de pH 10. La solubilité dans ces conditions et à la température de 20° C a été déterminé. Pour ceci nous avons préparé une solution aqueuse tamponnée au pH 10 (50% solution tampon), saturée en DNFB. Cette solution a été portée à 20° C pendant 24 heures. Une partie de celle-ci a été prélevée et polarographiée. Nous trouvons comme solubilité du DNFB la valeur de 24 mg/10 ml. Au pH 10 ces solutions donnent des polarogrammes très nets, ne présentant aucun maximum, ce qui évite l'emploi d'alcool polyvinylique.

Une étude de la stabilité a été alors effectuée sur des solutions contenant 10 mg de DNFB dans 25 ml tamponnés par 50% du tampon de pH 10. Les polarogrammes obtenus après 15, 30, 60 minutes, 2, 3 et 10 heures, présentent toujours trois sauts qui évoluent en fonction du temps. Après 24 heures, on observe seulement deux sauts. Ces derniers ne montrent plus aucune évolution durant les 24 heures suivantes. Ainsi ces solutions ne sont stables, à température ordinaire, qu'après 24 heures.

Nous avons alors étudié l'influence de la chaleur. Dans ce but, nous avons porté ces mêmes solutions à une température de 60° C pendant 15, 30, 60 minutes, 2 et 3 heures. Tous les polarogrammes effectués après refroidissement présentent dans ces conditions deux sauts parfaitement reproductibles. De plus ces deux sauts ont la même valeur de i_d que ceux de la solution conservée pendant 24 heures à température ordinaire.

En résumé, à partir de solutions ne contenant ni alcool absolu, ni alcool polyvinylique, il est possible par simple chauffage à 60° C pendant 15 minutes, d'obtenir, dans les conditions que nous venons d'exposer, des polarogrammes constitués de deux sauts nets et sans maximums. Au pH 10 on peut supposer une hydrolyse du DNFB en dinitrophénol[54,55]. Ce dernier, après une analyse polarographique a donné deux sauts aux mêmes potentiels que ceux de DNFB. Pourtant cette expérience n'est pas entièrement satisfaisante car il est peu probable que l'hydrolyse soit quantitative.

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V. DOSAGE POLAROGRAPHIQUE DU DNFB

Nous avons mis au point deux modes opératoires pour le dosage du DNFB par polarographie:

Premier mode opératoire (au pH 5)

Deux prises de DNFB, l'une de 180 mg et l'autre de 120 mg, sont dissoutes dans un peu d'alcool absolu dans deux ballons jaugés de 100 ml. 10 ml de chacune de ces solutions sont placés dans deux autres ballons de 100 ml. On ajoute 10 ml d'alcool absolu, 50 ml d'une solution tampon au pH 5 et on complète le volume avec de l'eau bidistillée. On obtient ainsi deux solutions de DNFB avec des concentrations de 18 et 12 mg/100 ml.

Par dilutions successives à l'aide d'une microburette et en respectant la composition des solutions (20% d'alcool et 50% de tampon au pH 5) on obtient les concentrations de 9, 6, 3 et 1 mg/100 ml.

Les concentrations de 71, 81, 91 et 93 mg/100 ml ont été préparées par pesées directes.

Avant de passer ces solutions au polarographe, on ajoute deux gouttes d'une solution d'alcool polyvinylique à 0.5% (préparée en dissolvant 1 g d'alcool dans 200 ml d'eau bidistillée; chauffer doucement pendant 10 minutes pour faciliter la dissolution et filtrer). Pour chasser l'oxygène, on fait barboter dans les solutions un courant d'hydrogène, durant 10 minutes, avant de les polarographier.

Le temps de chute de la goutte de mercure est de 2.94 sec et sa masse égale à 2.72 mg/sec. La hauteur de la colonne de mercure est de 17 cm.

Par ce mode opératoire, on peut doser le DNFB à des concentrations variant de 0.1 à 8.1 mg/10 ml (soit $5.37 \cdot 10^{-5}$ à $4.35 \cdot 10^{-3}$ molaire). Pour des concentrations plus fortes, les i_d ne sont plus une fonction linéaire de la concentration. La quantité minimum dosable est 0.1 mg/10 ml ou 1 γ/0.1 ml, ce qui est réalisable si l'on utilise la microcuve. La détermination au pH 10 est plus précise

Second mode opératoire (au pH 10)

Une prise de 100 mg de DNFB est traitée dans un bécher par 90 ml d'un mélange, à volume égal, (eau bidistillée-solution tampon de pH 10). On chauffe pendant 30 à 45 minutes à 60° C. La solution refroidie est mise dans un ballon jaugé de 100 ml et le volume complété avec le mélange eau bidistillée-solution tampon au pH 10.

Les autres prises sont préparées par dilutions successives à l'aide d'une microburette, le volume étant toujours complété à 10 ml avec le mélange eau-tampon. Les autres conditions du dosage sont les mêmes qu'au pH 5.

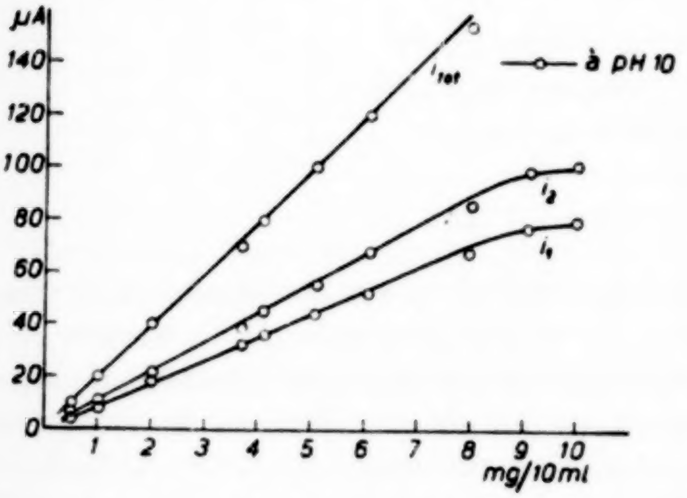

Fig. 1. Courbes d'étalonnage du DNFB au pH 10.

TABLEAU III

Conc. de DNFB en mg/10 ml	*Conc. molaire*	i_1 (μA)	i_2 (μA)	i_{tot} (μA)	i_1/i_2	i_1/k	i_2/k	i_{tot}/k
0.01	$5.37 \cdot 10^{-6}$	0.096	—	—	—	7.50	—	—
0.05	$2.68 \cdot 10^{-5}$	0.510	0.54	1.05	0.95	8.00	8.50	16.50
0.10	$5.37 \cdot 10^{-5}$	0.840	1.02	1.86	0.84	6.60	8.00	14.60
0.50	$2.68 \cdot 10^{-4}$	4.500	5.20	9.70	0.87	7.10	8.20	15.30
1.00	$5.37 \cdot 10^{-4}$	8.800	10.50	19.30	0.84	6.90	8.25	15.15
2.00	$1.07 \cdot 10^{-3}$	18.000	21.70	39.70	0.83	7.07	8.55	15.62
4.10	$2.20 \cdot 10^{-3}$	35.400	45.10	80.50	0.79	6.77	8.60	15.37
5.10	$2.77 \cdot 10^{-3}$	44.400	55.30	99.70	0.81	6.75	8.40	15.15
6.10	$3.27 \cdot 10^{-3}$	52.000	68.10	120.10	0.77	6.69	8.70	15.39
8.00	$4.29 \cdot 10^{\cdot 3}$	67.200	85.70	152.90	0.78	6.55	8.40	14.95
9.10	$4.88 \cdot 10^{-3}$	77.000	93.00	175.00	0.78	6.62	8.45	15.07
10.00	$5.37 \cdot 10^{-3}$	79.000	100.00	179.00	0.79	6.17	7.84	14.01

La courbe d'étalonnage obtenue est donnée dans le Tableau III et la Fig. 1.

Dans ce cas, le dosage est réalisable pour des concentrations variant de 10 γ à 8 mg/10 ml (soit $5.37 \cdot 10^{-6}$ à $4.29 \cdot 10^{-3}$ molaire). La quantité minimum dosable est de 0.01 mg/10 ml ou 0.1 γ/0.1 ml. L'erreur commise est de 7% maximum et 4% minimum. La sélectivité polarographique est bonne car les valeurs des $E_{1/2}$ sont faibles.

VI. DÉTERMINATION DU NOMBRE D'ÉLECTRONS (*n*) ÉCHANGÉS SUR L'ÉLECTRODE À GOUTTE

n peut être déterminé notamment par les méthodes suivantes:

(1) *La formule de Heyrovsky-Ilkovic*[47]

$$n = \frac{0.0591}{E_{1/2} - E} \log \frac{i}{i_d - i} \quad \dots\dots\dots\dots\dots\dots \quad (1)$$

est valable uniquement pour les réactions réversibles. Ce, qui n'est pas le cas ici.

(2) *La formule d'Ilkovic*

$$n = \frac{i_d}{605 \,.\, c \,.\, D^{1/2} \,.\, m^{2/3} \,.\, t^{1/6}} \quad \dots\dots\dots\dots\dots\dots \quad (2)$$

ou
c = concentration en millimol/litre
D = constante de diffusion en $\mathrm{cm}^2.\mathrm{sec}^{-1}$
m = masse de mercure en mg/sec
t = temps de goutte en sec
i_d = courant de diffusion en μA.

Pour calculer *n* par cette formule il faut connaître *D*. Cette constante peut être déterminée par des mesures de conductibilité en se basant sur la loi de FICK[48].

Mais cette détermination présente des difficultés. En général on attribue au corps étudié une constante connue d'un autre corps qui est de grandeur et de structure moléculaire semblable[49] ce qui d'ailleurs constitue l'inconvénient de cette méthode— sur laquelle nous reviendrons plus loin à titre de comparaison.

(3) *Détermination de* n *par microcoulométrie*[50].

Nous avons appliqué la méthode de REYNOLDS ET SHALGOSKY[50]. Ces auteurs effectuent une microélectrolyse sur 0.2 à 0.4 ml de solution dans une microcuve polarographique, avec, comme cathode un capillaire à goutte de mercure. Le nombre d'électrons *n* est donné par l'expression

$$n = \frac{\mathrm{M}.t}{\mathrm{F}} \cdot \frac{i_o + t_t}{i_o - i_t} \cdot \frac{ic}{2.\mathrm{V}._c}$$

ou
M = Poids moléculaire
t = Durée de l'électrolyse
i_o = Courant au début de l'électrolyse
i_t = Courant après t secondes d'électrolyse
V = Volume de la solution
c = Concentration de la solution

Partie expérimentale

Détermination de n *au pH* 10 *par microcoulométrie*

Afin que la différence $i_o - i_t$ soit sensible, il est avantageux d'effectuer l'électrolyse sur un petit volume de solution. C'est pourquoi nous avons construit une microcuve permettant l'emploi de petits volumes de liquide (0.2 à 0.5 ml). Les résultats pour le pH 10 sont portés dans le Tableau IV (1er saut) et dans le Tableau V (2ème saut).

TABLEAU IV

Conc. de DNFB (γ/1 ml)	*pH*	*E. const. employé (volt)*	*Temps de l'électro-lyse (sec)*	*Volume de la solution (ml)*	i_o^1 *(μA)*	i_t^1 *(μA)*	n_1
186.1	10	1.2	1200	0.3	8.4	7.7	4
186.1	10	1.2	1200	0.3	8.4	7.7	4
186.1	10	1.2	1200	0.3	8.4	7.7	4

TABLEAU V

Conc. de DNFB (γ/1 ml)	*pH*	*E. const. employé (volt)*	*Temps de l'électro-lyse (sec)*	*Volume de la solution (ml)*	i_o^2 *(μA)*	i_t^2 *(μA)*	n_2
186.1	10	1.2	1200	0.3	10.5	9.65	5.1
186.1	10	1.2	1200	0.3	10.5	9.70	5.4
186.1	10	1.2	1200	0.3	10.5	9.65	5.1

Remarque: Pour des temps d'électrolyse supérieurs à 1200 sec les résultats sont altérés. Les auteurs de cette méthode microcoulométrique recommande d'ailleurs de ne pas dépasser vingt minutes.

En conclusion, nous pouvons dire que la solution de DNFB à pH 10 demande pour sa réduction 4 électrons pour le premier saut et 5 électrons pour le second.

Détermination de n *au pH* 10 *par la formule d'Ilkovic*

Ainsi que nous l'avons dit sous chiffre(2), nous allons maintenant, à titre de comparaison, calculer *n* par la formule d'Ilkovic.

Pour ce faire, nous utiliserons la constante de diffusion de l'ion benzoate ($D = 8.28 \cdot 10^{-6}$). Les calculs ont été faits sur les polarogrammes obtenus avec des solutions de concentration variable en DNFB et contenant 50% de solution tampon de pH 10. Le temps de chute (t) de la goutte de mercure est de 2.94 sec et sa masse (m) de 2.727 mg/sec. Un exemple de tels polarogrammes est donné dans la Fig. 2. Les valeurs de *n* ainsi obtenues sont reproduites dans le Tableau VI.

Les valeurs moyennes *n* sont donc:

$$n_1 = 3.95;\ n_2 = 4.96;\ n_{tot} = 8.92.$$

n devant être un nombre entier, on peut admettre que 4 électrons interviennent dans le premier saut, 5 dans le second et naturellement 9 dans la réduction globale, ce qui correspond aux résultats obtenus précédemment.

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TABLEAU VI

Conc. de DNFB en mg/100 ml	*Conc. molaire*	i_1 *(µA)*	n_1	i_2 *(µA)*	n_2	i_{tot} *(µA)*	n_{tot}
37.22	$2 \cdot 10^{-3}$	31.50	3.88	38.7	4.76	70.20	8.62
20.00	$1.07 \cdot 10^{-3}$	18.00	4.12	21.7	4.97	39.70	9.19
41.00	$2.20 \cdot 10^{-3}$	35.40	3.96	45.1	5.04	80.50	9.00
51.00	$2.73 \cdot 10^{-3}$	44.40	3.99	55.3	4.97	99.70	8.96
61.00	$3.27 \cdot 10^{-3}$	52.00	3.90	68.1	5.11	120.10	9.01
80.00	$4.29 \cdot 10^{-3}$	67.20	3.85	85.7	4.21	152.90	8.76

Détermination de n *au pH 5 par la formule d' Ilkovic*

Nous compléterons notre étude sur la valeur de *n* par les calculs faits sur le polarogramme d'une solution de DNFB 10^{-3} molaire, contenant 50% de tampon de pH 5 et 20% d'alcool absolu. Comme déjà dit, il faut ajouter dans ce cas 5 gouttes d'une solution d'alcool polyvinylique à 0.2% pour supprimer les maximums. Le temps de goutte et la masse d'une goutte de mercure sont les mêmes qu'auparavant. Les résultats sont consignés dans le Tableau VII.

TABLEAU VII

		n
i_1 (µA)	16.05	3.95
i_2 (µA)	12.15	2.99
i_{tot} (µA)	28.20	6.94

Les valeurs de *n* pour le premier et le second saut sont respectivement 3.95 et 2.99. Ces résultats trop faibles sont dus à l'emploi d'alcool et d'alcool polyvinylique qui modifient la constante de diffusion.

Devant comparer le DNFB à un corps semblable, nous avons choisi le *m*-dinitrobenzène, déjà étudié par PEARSON[51]. Ce dernier trouve que le *m*-dinitrobenzène, en pH légèrement acide ou alcalin, produit deux sauts, chacun faisant intervenir 4 électrons.

Une solution de *m*-dinitrobenzène 10^{-3} molaire, contenant 50% de tampon de pH 5 et 20% d'alcool absolu a été polarographiée en présence d'alcool polyvinylique. Nous donnons les résultats dans le Tableau VIII.

TABLEAU VIII

		n *(trouvé)*	*n* *(réel)*
i_1 (µA)	11.7	2.88	4
i_2 (µA)	11.25	2.71	4
i_{tot} (µA)	22.95	5.59	8

Remarque: PEARSON trouve pour le *m*-dinitrobenzène $n_1 = 4, n_2 = 4$. Nous obtenons $n_1 = 5, n_2 = 4$ sans qu'il nous soit possible d'expliquer cette divergence.

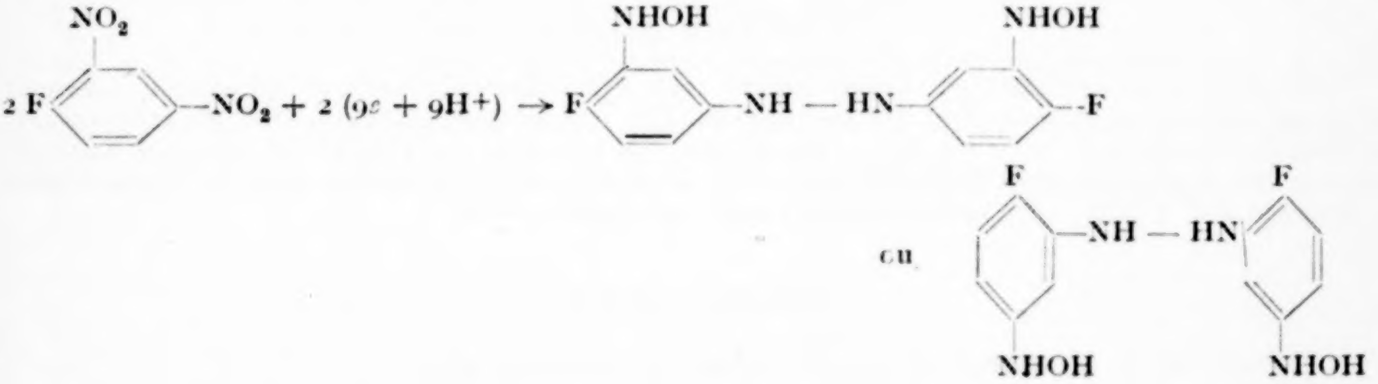
VII. CONCLUSIONS QUANT A LA VALEUR DE *n*

Au pH 5 et en présence d'alcool, la comparaison avec le *m*-dinitrobenzène, nous permet de conclure que le rapport i_1/i_2 est de 5/4.

Au pH 10 (sans alcools absolu et polyvinylique) les résultats trouvés, selon REYNOLDS, pour i_1 et i_2 étant respectivement de 4 et 5 électrons, le rapport i_1/i_2 est inversé: 4/5. Nous supposons que cette inversion est due à la présence d'alcool, car lorsque nous polarographions une solution de DNFB à pH 10 contenant 5% d'alcool pur, le rapport i_1/i_2 reprend la valeur 5/4. En outre, des polarogrammes obtenus des solutions contenant le dinitrophenol, tamponné à pH 10 en présence et en l'absence d'alcool donnent toujours deux sauts dont le rapport i_1/i_2 est de 4/5 (pas d'inversion). Il faut admettre donc que l'inversion dans le cas de DNFB en présence d'alcool est due probablement à la formation de dinitrophenol.

Pour expliquer la réduction du DNFB nous nous baserons sur les travaux de LINGANE[52]. Cet auteur a trouvé que la réduction coulométrique de l'acide picrique en milieu chlorhydrique 0.1*N* exige 17 électrons. Deux fonctions nitro- se réduisent en amines, absorbant 6 électrons chacune, la troisième fonction nitro-, en para, se réduit en fonction hydrazo-, ce qui nécessite encore 5 électrons.

La réduction du DNFB en pH légèrement acide ou alcalin demande 9 électrons. 4 sont nécessaires pour la réduction d'une fonction nitro- en hydroxylamine et 5 pour la réduction de la deuxième fonction nitro- en une fonction hydrazo- qui se condense avec une même fonction d'une autre molécule de DNFB réduite, suivant l'équation:



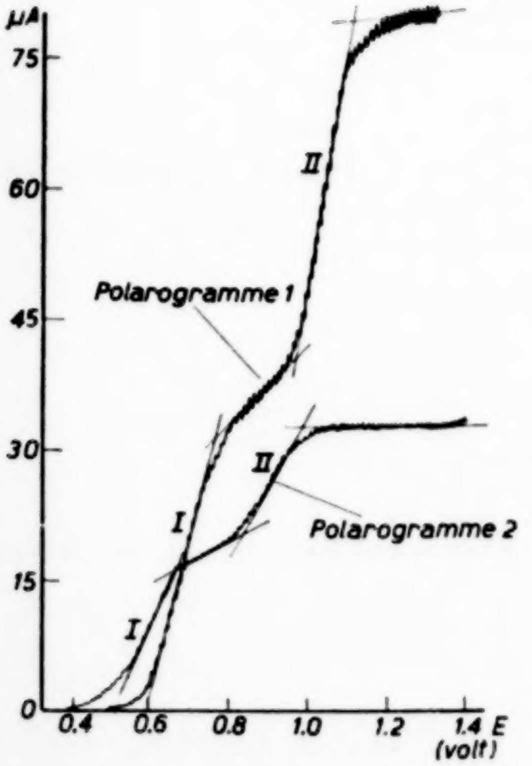


Fig. 2. Courbes polarographiques du DNFB à deux concentrations différentes.

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Etude logarithmique

L'étude logarithmique faites sur les courbes du Fig. 2 montre que les réactions ne sont pas réversibles et permet de supposer que chaque saut correspond à une seule réaction de réduction.

Conditions d'obtention des polarogrammes

Polarogramme no. 1.

DNFB $2 \cdot 10^{-3} M$, tamponné au pH 10.

$E^1_{1/2} = 0.68$ volt; $E^2_{1/2} = 1.03$ volt

$i^1_d = 31.5$ μA; $i^2_d = 38.7$ μA.

Polarogramme no. 2.

DNFB $10^{-3} M$ tamponné au pH 5 en présence de 20% d'alcool. (Le maximum est supprimé par 4 gouttes d'une solution d'alcool polyvinylique à 0.2%.)

$$E^1_{1/2} = 0.59 \text{ volt}; \qquad E^2_{1/2} = 0.91 \text{ volt}$$
$$i^1_d = 16.05\ \mu\text{A}; \qquad i^2_d = 12.15\ \mu\text{A}.$$

RÉSUMÉ

Après une étude polarographique et un dosage du dinitrofluorobenzène à différents pH et la détermination du nombre d'électrons échangés (*n*) des courbes d'étalonnage ont été établies au pH 5 et 10.

Elles permettent de doser la DNFB jusqu'à une concentration de 1 γ par ml avec une précision de 4 à 7%.

Selon le pH, la courbe présente 2 ou 3 sauts. Les $E_{1/2}$ des 2 premiers sont inférieurs à 1 volt.

SUMMARY

After polarographic study and determination of dinitrofluorobenzene at varying pH and determination of a number of electron exchanges (*n*), standardization curves have been constructed at pH 5 and 10. They allow the estimation of DNFB to a concentration of 1γ/ml with a precision of 4-7%. The curve shows 2 or 3 leaps, according to pH. The $E_{1/2}$ of the first two are less than 1 volt.

ZUSAMMENFASSUNG

Nach einer polarographischen Untersuchung und einer Bestimmung von Dinitrofluorobenzol bei verschiedenen pH-Werten und der Bestimmung der Anzahl der ausgetauschten Elektronen (*n*), wurden die Eichkurven bei pH 5 und 10 ausgeführt. Sie erlauben das DNFB bis zu einer Konzentration von 1 γ/ml mit einer Präzision von 4-7% zu bestimmen. Je nach pH weist die Kurve 2 oder 3 Sprünge auf. Die $E_{1/2}$ der ersten beiden liegen unterhalb 1 Volt.

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BUCHBESPRECHUNG

Die Organische Analyse, von K. H. Bauer, 3. ergänzte und erweiterte Auflage, bearbeitet von H. Moll, Akademische Verlagsgesellschaft Geest und Portig K.G., Leipzig, 1954, 628 Seiten, 27 Figuren.

Von dem verdienstvollen Buch von K. H. Bauer, der diesem Werk seine letzten Lebensjahre widmete und in ihm eine reiche Erfahrung niederlegte, ist nunmehr in verhältnismässig kurzer Zeit eine überarbeitete und ergänzte 3. Auflage erschienen, die wiederum von H. Moll, einem Schüler von K. H. Bauer, besorgt wurde. Es ist gar keine Frage, dass die vielseitige organische Analyse als notwendige Hilfe zur Erkennung und Identifizierung der bunten Stoffwelt organischer Verbindungen angesichts ihrer hohen praktischen Bedeutung in Unterricht und Fachliteratur erst in den letzten Jahren die ihr gebührende Beachtung gefunden hat. Der Nutzen des Buches von Bauer-Moll liegt vor allem darin, dass das Hauptgewicht auf wohl ausgewählte, qualitativ und quantitativ verwendbare Gruppenreaktionen bei den wichtigsten Stoffklassen und auf die Beschreibung zahlreicher, häufig in der Praxis vorkommender Verbindungen gelegt wird (weit über 700 weist das Sachregister aus), während die Elementaranalyse — wofür andere Anleitungen zur Verfügung stehen — zurücktritt.

Die übersichtliche Stoffanordnung in 27 Kapiteln umfasst zunächst alle wichtigen Substanztypen mit bestimmten funktionellen Gruppen, anschliessend dann eine Reihe von Naturstoffklassen. So sind u.a. Purine, Proteine, Fette, Äther. Öle, Harze, Glykoside, Alkaloide, Sterine, Gallensäuren und Vitamine beschrieben, unter denen pharmazeutisch wichtige Vertreter mitunter besonders liebevoll dargestellt sind. Man kann sich auch über manche Raritäten, wie z.B. Drachenblut, Einreibemittel, Gheddawachs, Hasen- und Pferdefett, Intensivsüssstoff, Äther, Ölschwefel, Seifenwurzel und Süssmost analytisch orientieren. Ebenso fanden eine Reihe von Arzneimittel-Spezialitäten Aufnahme, wie Kodan-Tinktur, zahlreiche Sulfonamide, Lanogen, Lysol, Noctal, PAS, Quartamon, Sajodin, Vioform, Vulnalin u.a. Es folgen dann noch zwei kurze Abschnitte über Chromatographie und Papierchromatographie, die allerdings keine Arbeitsvorschriften enthalten, und ein nützliches, von L. Kofler selbst noch verfasstes Kapitel über die Verwendung des Mikroskops zur Kennzeichnung organischer Stoffe und Stoffgemische. Die genügend ausführlich gebrachten Arbeitsvorschriften und Gruppenreaktionen sind noch mit zahlreichen Literaturangaben belegt, vor allem aus pharmazeutischen und analytischen Zeitschriften.

Es erscheint dem Rezensenten müssig zu sein, die getroffene Stoffauswahl kritisieren zu wollen. Trotz der umfangreichen und überlegten Liste der Verbindungen werden wohl für den einen oder anderen Benutzer noch Wünsche offen bleiben. Hier muss ein Buch der vorliegenden Art einen goldenen Mittelweg gehen. Überdies werden in diesem Zusammenhang hoffentlich Neuauflagen für Auflockerung und Modernisierung sorgen. So wäre beispielsweise eine Überarbeitung der Analytik von schwefelhaltigen organischen Verbindungen zu empfehlen, die neuerdings eine immer grössere Bedeutung gewinnt und die sich doch etwas ausführlicher auch auf Disulfide, Sulfide, Rhodanide und Senföle erstrecken sollte. Thiole und Disulfide können, auch aus praktischen Gründen, bei Nachweis- und Bestimmungsmethoden nur gemeinsam betrachtet werden.

Wie Stichproben zeigten, sind die Angaben über die physikalischen Konstanten der beschriebenen Verbindungen im allgemeinen verlässlich (der Schmp. von L-Asparaginsäure liegt bei 270-271° C und nicht bei 226°, der Schmp. von Bernsteinsäure bei 182.8° C und nicht bei 128.8°). Im Aminosäure-Kapitel entspricht es nicht mehr der gegenwärtigen Gepflogenheit, wenn die in der Natur vorkommenden α-Aminosäuren (leider fehlt das wichtige Methionin!), die bekanntlich L-Konfiguration besitzen, je nach Drehungssinn als d- bzw. l-Verbindung gekennzeichnet werden. Diese Verwendung der Präfixe ist heute überholt. L-Cysteinhydrochlorid sollte zweckmässigersweise nur als kristallwasserhaltiges Salz gehandhabt werden. Die Angaben über die Kristallisation des schwerlöslichen L-Cystins können zu Irrtümern Anlass geben. Bei der Ninhydrin-Reaktion auf Aminosäuren wäre auch noch auf deren mangelhafte Spezifität hinzuweisen.

Das inhaltsreiche und kritisch geschriebene Buch wird bei der in Wissenschaft und Praxis oft auftauchenden Notwendigkeit der Kennzeichnung und Charakterisierung organischer Verbindungen ein nützlicher Führer sein, vor allem dann, wenn keine umfangreiche Fachbücherei zur Verfügung steht.

A. Schöberl (Hannover)

SIMPLE INSTRUMENT FOR TITRIMETRY WITHOUT INDICATORS GAS PRESSURE END-POINT TECHNIQUE

VIII. ACID-BASE REACTIONS*

by

OTTO RICHARD GOTTLIEB

Ornstein and Cia., Rio de Janeiro (Brazil)

The end-point of a volumetric analysis is generally determined by a visual change, observed in the liquid titrated. Because in relatively few cases the titration reaction itself is accompanied by a distinct color change, an end-point indicator is usually added to the system. If no suitable indicator is available, if the color change of any known indicator is too vague or if the sample solution is colored or contains solid material in suspension, recourse must be taken to instrumental analysis, which implies the existence of expensive apparatus in the laboratory.

The present investigation was made to supply the analyst with a reasonably general titrimetric technique for the cases mentioned above, which requires only very simple laboratory equipment.

In volumetric analysis, any property of the system which changes appreciably at the equivalence point, may be used for the detection of this point. The property involved in the present work is the pressure change of the closed system above the solution titrated at the equivalence point. This pressure change can be brought forth by gas evolution or gas absorption. Thus the end-point can be located, in different instances, (a) when gas evolution (due to reaction between sample and titrating solutions) ceases at the equivalence point, (b) when gas evolution (due to reaction between excess titrant and an auxiliary reagent) starts at the equivalence point, (c) when gas absorption (due to reaction between excess titrant and a gas present in the atmosphere above the reaction mixture) starts at the equivalence point.

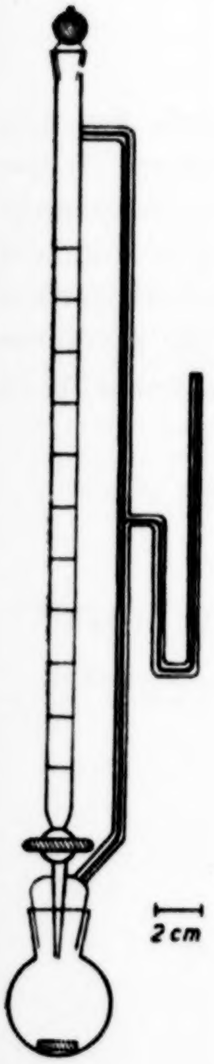

Fig. 1

Several different instruments, easily assembled, may be designed for this kind of end-point detection. Only one of them is described in this paper (Fig. 1).

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* The previous papers of this series were presented at the X and XI Brazilian Congresses of Chemistry, held respectively in Rio de Janeiro, July 1952 and São Paulo, July 1954, and will appear in *Anais da Associação Brasileira de Química* under the title: Dispositivo simples para titrimetria sem indicadores I. Acidimetria e alcalimetria, II. Determinaçao do ion sulfato, III. Determinaçao do ion nitrito, IV. Determinaçao do ion nitrato, V. Permanganimetria em meio alcalino, VI. Iodatometria, VII. Titrímetro automático registrador.

DESCRIPTION OF INSTRUMENT

The titration vessel is a 50 ml flask, provided with a hollow glass stopper, through which passes the tip of a 10 ml buret and a capillary tube, which connects the flask and the top of the buret. The upper end of the buret is closed with a hollow glass stopper, provided with a small hole on its side. This hole corresponds to a hole of the same size on the wall of the buret. By a slight rotatory movement of the stopper one can make the two holes coincide or not, in order to open or to close the apparatus. The capillary tube is connected with an U-tube, which contains a colored liquid. The bore of this capillary tube is about 1 mm for titrations involving 0.05 to 0.5*N* solutions. A magnetic stirrer provides stirring, which is always necessary.

ACIDIMETRY

Titration of acid with hydroxide

In titrating acid with alkaline hydroxide solutions (Table I), as long as the reaction of the sample remains acid, there should be no volume change of the system. (If the sodium hydroxide solution contains a small amount of carbonate, which is frequently the case, what really will be observed is, that before the end-point every drop of standard solution gives rise to a slight gas evolution.) Because alkaline solutions absorb carbon dioxide, any excess of hydroxide in the titration vessel will be followed by a volume reduction of the system. Consequently gaseous carbon dioxide serves as indicator in this titration.

TABLE I

TITRATION OF HCl SOLUTION WITH NaOH SOLUTION

HCl		*NaOH*			
N	*ml taken*	*N*	*Procedure 1*	*ml consumed indic. phenolpht.*	*Δ %*
0.5	5.00	0.5	4.99		
0.5	5.00	0.5	4.97		
0.5	5.00	0.5	4.97		
			mean 4.98	mean 4.99	—0.2
0.1	5.00	0.1	5.06		
0.1	5.00	0.1	5.05		
0.1	5.00	0.1	5.07		
			mean 5.06	mean 5.08	—0.4
0.05	5.00	0.05	5.04		
0.05	5.00	0.05	5.01		
0.05	5.00	0.05	5.03		
			mean 5.03	mean 5.02	+0.2

Procedure 1

Transfer 5.00 to 10.00 ml of the acid sample solution to the titration flask, breath into the latter for a fraction of a second and connect it with the buret. Titrate with standard hydroxide solution, stirring the mixture by means of the magnetic stirrer. Approaching the end-point proceed as follows: Close the apparatus (turning the stopper on top of the buret), introduce one drop of standard solution

into the flask, observe the direction of the displacement of the liquid in the U-tube after 30 seconds, open the apparatus to re-establish atmospheric pressure, close and repeat until the liquid in the U-tube indicates a contraction in the volume of the system. After the addition of each drop no drop fragment must remain suspended from the buret tip.

Titration of acid with carbonate

In titrating acid with alkaline carbonate solutions (Table II), every drop of the reagent gives rise to gas evolution. After the end-point has been reached, gas evolution ceases and in presence of excess carbonate carbon dioxide absorption begins.

TABLE II

TITRATION OF H_2SO_4 SOLUTION WITH Na_2CO_3 SOLUTION

H_2SO_4		Na_2CO_3			
N	*ml taken*	*N*	*Procedure 2*	*ml consumed indic. methylorange*	Δ %
0.1	5.00	0.1	4.83		
0.1	5.00	0.1	4.82		
0.1	5.00	0.1	4.84		
0.1	5.00	0.1	4.83		
0.1	5.00	0.1	4.85		
			mean 4.83	mean 4.82	+0.2

Procedure 2

Transfer 5.00 to 10.00 ml of the acid sample solution to the titration flask and titrate with standard carbonate solution stirring the mixture by means of the magnetic stirrer. Approaching the end-point wait until nearly all the gas has been expelled, then proceed as follows: Close the apparatus, introduce one drop of standard solution into the flask, observe the displacement of the liquid in the U-tube after one minute, open the instrument, close and repeat until the liquid in the U-tube no longer shows the regular increase in the volume of the system.

ALKALIMETRY

Titration of hydroxide with acid

In titrating an alkali hydroxide solution with standard acid (Table III), the latter

TABLE III

TITRATION OF NaOH SOLUTION WITH HCl SOLUTION

NaOH		*HCl*			
N	*ml taken*	*N*	*Procedure 3*	*ml consumed indic. phenolpht.*	Δ %
0.1	5.00	0.1	4.88		
0.1	5.00	0.1	4.89		
0.1	5.00	0.1	4.89		
0.1	5.00	0.1	4.90		
			mean 4.89	mean 4.88	+0.2
0.05	5.00	0.05	4.87		
0.05	5.00	0.05	4.87		
0.05	5.00	0.05	4.86		
			mean 4.87	mean 4.85	+0.4
0.01	5.00	0.01	5.00		
0.01	5.00	0.01	4.98		
			mean 4.99	mean 5.00	—0.2

will absorb some carbon dioxide from the air causing a slight volume reduction of the system. At the point where the sample turns acid some of the carbon dioxide absorbed (or pre-existent in the sample through contamination with carbonate) will be set free and a volume increase of the system can be observed. If for any reason (purity of the hydroxide solution, great speed in the titration) carbonate contamination is very small, a small quantity of sodium bicarbonate should be added to the sample. This is necessary, especially when titrating recently filtered alkaline earth hydroxides.

Procedure 3

Transfer 5.00 to 10.00 ml of the hydroxide sample solution to the titration flask and titrate with standard acid solution, stirring the mixture by means of the magnetic stirrer. Approaching the end-point proceed as follows: Close the apparatus, introduce one drop of standard solution into the flask, observe the displacement of the liquid in the U-tube after 1 minute, close and repeat until the liquid in the U-tube indicates an increase in the volume of the system.

Titration of carbonate with acid

In titrating an alkaline carbonate with standard acid (Table IV), half of the carbonate has to be transformed to bicarbonate before any gas evolution can be noted.)However, especially near the end-point, local superconcentration of acid often gives rise to a slight gas evolution. This effect can be eliminated by closing the system only after adding the drop of titrant.) From this first end-point on, every drop of the reagent gives rise to evolution of carbon dioxide. When all the bicarbonate has been destroyed, the gas evolution ceases and the volume of the system remains constant.

TABLE IV

TITRATION OF Na_2CO_3 SOLUTION WITH HCl SOLUTION

Na_2CO_3		HCl						
			ml consumed					
			First end-point			Second end-point		
N	*ml taken*	*N*	*Procedure 4*	*theoretical 9.62 . 2*	Δ %	*Procedure 4*	*indicat. methylor.*	Δ %
0.2	5.00	0.1	4.79			9.63		
0.2	5.00	0.1	4.77					
0.2	5.00	0.1	4.75					
0.2	5.00	0.1	4.78			9.62		
0.2	5.00	0.1	4.85					
0.2	5.00	0.1	4.79					
0.2	5.00	0.1	4.81			9.64		
0.2	5.00	0.1	4.78					
0.2	5.00	0.1	4.81					
			mean 4.79	4.81	-0.4	mean 9.63	9.62	+0.1

Procedure 4

Transfer 5.00 to 10.00 ml of the carbonate sample solution to the titration flask and titrate slowly with standard acid solution, stirring the mixture briskly by means of the magnetic stirrer. Approaching the first end-point proceed as follows: Open the apparatus, introduce one drop of standard solution into the flask, wait approximately 5 seconds, close, observe the displacement of the liquid in the U-tube, open, add another drop and repeat until the liquid in the U-tube indicates a volume increase of the system. Proceed with the titration using *Procedure 2* to determine the second end-point.

Titration of bicarbonate with acid

In titrating bicarbonate with standard acid solution, every drop of the reagent gives rise to gas evolution. After the end-point has been reached gas evolution ceases.

Procedure 5

Transfer 5.00 to 10.00 ml of the bicarbonate sample solution to the titration flask and titrate with standard acid solution, stirring the mixture by means of the magnetic stirrer. Follow *Procedure* 2 to determine the end-point.

Titration of mixtures of bicarbonate and carbonate or carbonate and hydroxide with acid

If in the titration of carbonate, as given above, the amount of acid used to reach the first end-point is equal to half the amount used to reach the second end-point, the sample contains neither hydroxide nor bicarbonate. But if the former amount is less than half the latter one, the sample contains also bicarbonate. If, on the contrary, the first gas evolution starts more than half way through to the second, the sample is a mixture of hydroxide and carbonate. Therefore *Procedure* 4 is useful for the analysis of both mixtures.

Precision and accuracy

As the tables show, in the instances studied, precision is comparable with that attainable in normal indicator end-point titrations.

The accuracy of every reaction studied was proved, performing a series of gas pressure end-point titrations in presence of indicators. With exception of the titration of acid with alkali in presence of carbon dioxide using phenolphtalein as indicator, the same drop which indicated the end-point by the gas pressure technique was also responsible for the color change of the indicator.

Concentration limit

The lower concentration limit, to which the gas pressure end-point technique can be applied in the particular type of apparatus described in this paper, depends on the gas volume still capable of giving a visible impulse to the liquid column in the U-tube. This gas volume, set free by a particular reaction, is determined by the volume of the titration solution added from the buret, and its strength. The gas set free by one drop (0.05 ml) of 0.01*N* titrating solution is still capable of affecting the height of liquid contained in capillary tubing of 1 mm bore. This same capillary tube is still useful in titrations involving *N* solutions, but from 0.5*N* upward a tube of greater internal diameter may be used.

DISCUSSION

The instrument is rather thermosensitive, and for this reason it should be kept in a laboratory not exposed to changes of temperature; also none of its parts should be touched excepting stopper and stopcock. The magnetic stirrer should not touch the titration flask. Whenever the apparatus is to be used for the analysis of solutions whose concentration is below 0.05N, greater precision is obtained if the titration flask is thermostated.

Since the buret tip is inaccessible no drop splitting is possible and the analysis must proceed with successive additions of regular increments of titrating solution.

In many titrations it is advisable to add the drops of titrating solution at fixed intervals of time or to wait until the atmospheric pressure is re-stablished in the interior of the apparatus before any further addition of standard solution. Thus the technique is more time consuming than a normal indicator end-point titration. This inconvenience is more than compensated by the fact, that the proposed technique makes it possible to titrate directly samples which would usually have to be pretreated owing to their color or to the coexistence of solids. The clarification of sample solutions to a point where a visual end-point can be observed with sufficient precision is generally accompanied by the risk of sample losses and is always more tedious and time consuming than the direct gas pressure titration.

The proposed technique can also be used with advantage when the known indicators give no sharp color change at the end-point. As it is based on the observation of a mechanical phenomenon, greater precision is obtained.

Attempts to develop new titrimetric methods fail sometimes, because no good indicators can be found. In these cases, the proposed gas pressure end-point technique is valuable, whenever one or more of the reaction products are gases or when one of the reagents is able to react rapidly and quantitatively with a third one developing a gas.

When mixtures of substances with identical chemical characteristics (*e.g.* alkalies, reducing substances) are titrated with reagents (*e.g.* acids, oxidants) to a color end-point, the result will represent often only the sum of the different substances present. If some constituents of the mixture develop gases with the titrant and others do not, the gas pressure end-point technique, used alone or in conjunction with the color end-point technique, will provide more information in one analysis, than the latter one alone.

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SUMMARY

Visual changes in the liquid titrated cannot always be used for the detection of the end-point in volumetric analysis. To help analysts who do not have at their disposal the more or less complicated and expensive instruments required to solve those cases, the present paper suggests a simple titrimetric technique. The direction of the pressure change (gas evolution or gas absorption) at the equivalence point, in a closed system above the solution titrated, is observed in an easily assembled glass apparatus. Results obtained with this technique in the solution of acidimetric and alkalimetric problems are reported. They are comparable in precision and accuracy to the values obtained by the usual indicator titrations. The apparatus described is useful for the analysis of 0.01N or more concentrated solutions.

RÉSUMÉ

Les titrations volumétriques avec indicateurs visuels ne sont pas toujours possibles. Pour aider les analystes, n'ayant pas à leur disposition les plus ou moins compliqués et coûteux appareils nécessaires dans ce cas, l'auteur propose une technique titrimétrique simple. Le point d'équivalence est

déterminé, en observant la direction du changement de pression (dégagement gazeux ou absorption) dans un système fermé au-dessus de la solution à titrer. Des résultats obtenus en alcali-acidimétrie au moyen de cette technique sont donnés; la précision est comparable à celle des méthodes usuelles, utilisant des indicateurs. L'appareil décrit convient au dosage de solutions 0.01 *N* ou plus concentrées.

ZUSAMMENFASSUNG

Volumetrische Titrationen mit Farbindikatoren sind nicht immer möglich. Um den Analytikern zu helfen, welche nicht die mehr oder weniger komplizierten und teuren Apparate zu ihrer Verfügung haben, die in diesem Falle notwendig sind, schlägt der Autor eine einfache titrimetrische Technik vor. Der Gleichgewichtspunkt wird bestimmt, indem man die Richtung der Druckänderung (Gasentweichung oder-adsorption) beobachtet in einem über der zu titrierenden Lösung angebrachten, geschlossenen System. Resultate von Alkali-Azidimetrie werden angegeben. Die Präzision kann mit derjenigen der üblichen Methoden verglichen werden, welche Indikatoren verwenden. Der beschriebene Apparat geht für Bestimmungen von 0.01 *N* oder konzentrierteren Lösungen.

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OXIDATIONS WITH ALKALINE PERMANGANATE USING FORMIC ACID FOR BACK-TITRATION

III. DETERMINATION OF LEAD AND THALLIUM

by

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Thallium is found associated with lead in its ores and in some lead alloys. Some of its reactions are similar to those of lead; thus thallous chloride, iodide, sulphide and chromate are precipitated in an analogous manner to the corresponding lead compounds. Since both lead and thallous compounds can be oxidized with potassium permanganate in alkaline media[1,2], it is interesting to study the oxidation of the two metals by that reagent and to find out whether they can be determined in presence of each other.

EXPERIMENTAL

(a) Potassium permanganate was prepared as recommended by STAMM[3].
(b) Solutions of lead were prepared by dissolving lead nitrate "Grade Analar" in twice distilled water. The lead content was determined potentiometrically using our previous method[1].
(c) Solutions of monovalent thallium were prepared from thallous acetate "laboratory B. D. H. grade" and thallous sulphate "laboratory Prolabo grade". The thallium content of the solutions was determined by precipitation as Tl_2CrO_4[4] and by titration with potassium permanganate in presence of 0.1*N* NaOH[2].

The experimental technique is the same as previously described[1].

RESULTS

(A) *Estimation of lead*

1. *Oxidation of bivalent lead with potassium permanganate and back titrating excess oxidant with formic acid*

It was previously shown[1] that Pb^{+2} could be determined by mixing with $KMnO_4$ in presence of 1*N* NaOH and Ba^{+2} ions equivalent to the $KMnO_4$ whereby the excess oxidant was then back-titrated with Pb^{+2} solution. Amounts of lead as low as 31 mg could be estimated by this method. In this investigation an attempt is made to determine smaller quantities of lead. The oxidation of Pb^{+2} is performed under the above conditions. After leaving the mixture for 5 minutes, the excess of $KMnO_4$ was estimated with formic acid of the appropriate concentration. The data shown in Table I represent the results obtained by the new procedure. From these results it is apparent that quantities of lead as low as 0.6 mg can be determined with fair accuracy.

TABLE I

ESTIMATION OF Pb^{+2} BY OXIDATION WITH $KMnO_4$ AND BACK TITRATING EXCESS WITH FORMIC ACID

Vol. and Normality of $KMnO_4$	*Normality of formic acid*	*Vol. and Normality of* Pb^{+2} *solution*	*mg Pb added*	*mg Pb found*	*Error %*
25 ml 0.1204*N*	0.03255*N*	3 ml 0.1202*N*	37.422	37.321	—0.27
,,	,,	1 ml ,,	12.474	12.432	—0.34
,,	,,	4 ml 0.03005*N*	12.474	12.442	—0.26
,,	,,	3 ml 0.01202*N*	3.742	3.760	0.48
,,	,,	1 ml ,,	1.247	1.252	0.43
,,	,,	0.5 ml ,,	0.624	0.620	—0.65

II. *Direct oxidation of bivalent lead with permanganate in presence of telluric acid*

It was previously shown[1] that the direct titration of plumbite with $KMnO_4$ in 0.1*N* NaOH yields Pb_3O_4, whence $KMnO_4$ becomes reduced to MnO_2. In this investigation the reaction is performed in presence of telluric acid, which as was shown by Tomiček[5], prevents the precipitation of MnO_2. However, addition of telluric acid precipitates lead tellurate which is readily oxidized by $KMnO_4$ to PbO_2 whereby the oxidant is reduced to manganate, even in 0.1*N* NaOH. As may be visualized from the data shown in Table II the results obtained approach the theoretical values calculated on this basis only in 0.1*N* NaOH. By raising the alkali concentration to 1 - 3*N* the end-points are attained earlier. These observations may be explained on the premise that lead tellurate apparently possesses a weaker reducing power than plumbite and, on account of its smaller solubility it yields in 0.1*N* NaOH solution Pb^{+2} sufficient to be oxidized to PbO_2 by the permanganate added. As the alkali concentration is raised, the solubility of lead tellurate increases and the reaction medium contains a mixture of plumbite and lead tellurate. Reduction of $KMnO_4$ yields then a mixture of MnO_2 and manganate, oxidation of Pb^{+2} possibly gives a mixture of PbO_2 and Pb_3O_4, leading to an early end-point (see Fig. 1 B). In presence of 3*N* NaOH, the first ml of $KMnO_4$ is reduced exclusively to MnO_2 but the green manganate colour appears after addition of the second ml.

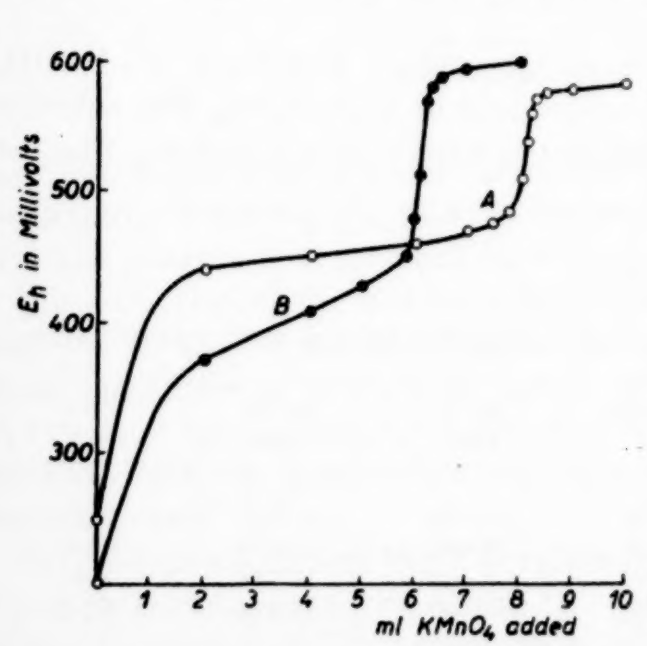

Fig. 1. 10 ml 0.02404*N* Pb^{+2} titrated with 0.1438*N* $KMnO_4$ in presence of telluric acid; (A) in 0.1*N* NaOH, (B) in 2*N* NaOH.

TABLE II

TITRATION OF Pb^{+2} WITH $KMnO_4$ IN PRESENCE OF TELLURIC ACID

Alkali conc.	*Max. inflec. per 0.1 ml $KMnO_4$*	*Theor. end-point*	*Exper. end-point*	*Error %*
5 ml 0.04808N Pb^{+2} titrated with 0.1438N $KMnO_4$:				
1N	27 mV	8.28 ml	6.95 ml	16.27
2N	20 ,,	8.29 ,,	5.95 ,,	28.07
10 ml 0.02404N Pb^{+2} titrated with 0.1438N $KMnO_4$:				
0.1N	30 mV	8.29 ml	8.05 ml	2.89
1N	37 ,,	8.29 ,,	7.45 ,,	10.12
2N	55 ,,	8.29 ,,	6.13 ,,	26.03
3N	54 ,,	8.29 ,,	4.98 ,,	39.88

(B) *Estimation of thallium*

Oxidation of Tl^+ with $KMnO_4$ and titrating excess with formic acid

As will be shown later (to be published) reduction of $KMnO_4$ with Tl^+ can be checked at the manganate state by Ba^{+2} ions. A procedure based upon this fact can be devised for the determination of Tl^+ ions. The process depends upon mixing Tl^+ with $KMnO_4$ in presence of 1N NaOH and Ba^{+2} ions. Addition of Tl^+ should be made slowly while stirring the permanganate solution and the excess oxidant titrated with formic acid. Table III includes results obtained by this method which is applicable to amounts of thallium as low as 0.9 mg with a maximum error of 0.55%.

Neither oxalic acid nor ferrous iron can be used for the estimation of excess $KMnO_4$ in acid medium, because thallic ions (as can be gathered from the high value of the redox potential of the system Tl^{+3}/Tl^+ in acid medium and which amounts to 1.25 volt[6]) can oxidize these reagents. This is apparent from the following experiments:

(a) 5 ml of $8.8 \cdot 10^{-3}N$ Tl^+ were added to 25 ml of 0.1261N $KMnO_4$ in presence of 2N NaOH in absence of Ba^{+2} ions. The mixture was then poured onto 30 ml of 0.1328N Fe^{+2} in 5N H_2SO_4. The excess ferrous iron was then titrated with 0.1261N $KMnO_4$ and required 6.60 ml.

(b) 5 ml of $8.8 \cdot 10^{-3}N$ Tl^+ were mixed with 25 ml 0.1261N $KMnO_4$ in 2N NaOH. The solution was then added to 50 ml of 0.1N oxalic acid in 3.6N H_2SO_4. The solution was then heated and the excess oxalic acid estimated with 0.1261N $KMnO_4$ when it consumed 14.7 ml.

TABLE III

ESTIMATION OF Tl^+ BY OXIDATION WITH $KMnO_4$ AND TITRATING EXCESS WITH FORMIC ACID

Vol. and Normality of $KMnO_4$	*Normality of formic acid*	*Vol. and Normality of Tl^+ added*	*mg Tl added*	*mg Tl found*	*Error %*
50 ml 0.1235N	0.1032	5 ml 0.088 N	44.966	45.141	0.30
25 ,, 0.1235N	0.1032	1 ml 0.088 N	8.993	9.028	0.30
25 ,, 0.1235N	0.0512	3 ml 0.0088N	2.698	2.710	0.40
25 ,, 0.1235N	0.0512	1 ml 0.0088N	0.899	0.904	0.55

(C) *An attempt to titrate lead and thallium in a mixture of both*

I. *Direct oxidation of Pb^{+2}-Tl^{+} mixture*

(i) Titration of a Pb^{+2}-Tl^{+} mixture in $0.1N$ NaOH with $KMnO_4$ without the addition of telluric acid results in the oxidation of both constituents: $Pb^{+2} \rightarrow Pb_3O_4$ and $Tl^{+} \rightarrow Tl^{+3}$ whence reduction of $KMnO_4$ proceeds absolutely to MnO_2. The behaviour of the mixture simulates that of the separate constituents, and as may be visualized from Fig. 2 the titration curve A, is characterized by a single inflection and the volume of $KMnO_4$ consumed in the titration corresponds to the simultaneous oxidation of Pb^{+2} and Tl^{+}. Theoretically however, as may be gathered from the redox potential values ($E_{\circ}(_{OH})$ Tl^{+3}/Tl^{+} = —0.05 volt and $E_{\circ}(_{OH})$ Pb_3O_4/PbO = 0.24 volt)[6], oxidation of Tl^{+} should take place prior to that of Pb^{+2}.

(ii) In $0.1N$ NaOH, and after precipitating lead as sulphate, Tl^{+} is oxidized together with some Pb^{+2}, apparently owing to the partial solubility of $PbSO_4$ in the reaction medium. By saturating the solution with Na_2SO_4, the oxidation of Pb^{+2} is only slightly minimized. When the alkalinity of the solution is made $1N$, most of the $PbSO_4$ dissolved and the mixture was oxidized as in case (i).

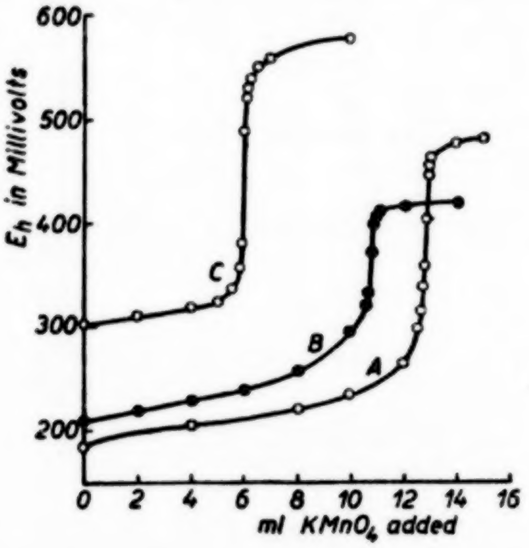

Fig. 2. Titration of 10 ml $0.1202N$ Pb^{+2} + 10 ml $0.0517N$ Tl^{+}
(A) with $0.1204N$ $KMnO_4$ in $0.1N$ NaOH
(B) with $0.1438N$ $KMnO_4$ in $1N$ NaOH
(C) with $0.1438N$ $KMnO_4$ in $0.1N$ NaOH.
Pb^{+2} precipitated as $PbSO_4$ in presence of telluric acid.

(iii) By performing the titrations in $0.1N$ NaOH and in presence of telluric acid, both Pb^{+2} and Tl^{+} are simultaneously oxidized. Although Pb^{+2} reduces MnO_4^{-} under these conditions to MnO_4^{-2}, the green manganate colour was only observed near the end of the titration, MnO_4^{-2} being further reduced by Tl^{+} present. When all Tl^{+} has been oxidized, the green colour appears and the end-points are associated with considerable errors.

(iv) By precipitating Pb^{+2} as sulphate in presence of telluric acid, its interference is greatly minimized so long as the Tl^{+} concentration is as high as 31 mg (see Fig. 2 C). When the amount of Tl^{+} is small (as is usually encountered in analysis), and a suitable

References p. 114

diluted $KMnO_4$ solution is used, considerable errors due to the interference of lead are observed. This is apparent from the fact, that the excess volume of $KMnO_4$ consumed by lead will increase considerably by diluting the titrant. Indeed it was observed that the precipitate obtained by adding sodium sulphate and telluric acid reduces permanganate very slowly.

Reactions performed under (i) are more or less rapid but need ∿ 5 minutes at the end-point. Those performed under (ii) are slower than (i), needing ∿ 3 minutes at the beginning of titration and 7-8 minutes near the end. After precipitating Pb^{+2} as $PbSO_4$ in presence of telluric acid and using NaCl as a catalyst, equilibria are attained 1 and 3 minutes at the beginning and at the end of the reaction respectively.

TABLE IV

TITRATION OF Pb^{+2}-Tl^{+} MIXTURE WITH $KMnO_4$ IN ABSENCE OF TELLURIC ACID

$Pb^{+2} \rightarrow Pb_3O_4$ $Tl^{+} \rightarrow Tl^{+3}$

Tl^{+} = (0.0517*N*• and 0.1262*N* † Pb^{+2} = 0.0601*M*

Alkalinity	*Max. inflec. per 0.1 ml $KMnO_4$ in mV*	*Vol. of Pb^{+2}*	*Solution Tl^{+}*	*Theor. end-point Pb^{+2}*	*Theor. end-point Tl^{+}*	*Exp. end-point in ml*	*Error %*
		in ml		*in ml*			
Using 0.1204*N* $KMnO_4$, NaCl as catalyst:							
0.1*N*	65	10	10	5.55	7.16•	12.77	0.47
Using 0.1438*N* $KMnO_4$, Pb^{+2} precipitated as sulphate:							
1*N*	41	10	10	4.64	5.99•	10.67	0.37
0.1*N* (1 g Na_2SO_4)	57	10	5	4.64	7.31 †	9.5	30.0
0.1*N* (2 g Na_2SO_4)	46	10	5	4.64	7.31 †	9.26	26.6
0.1*N* (saturated with Na_2SO_4)	40	10	5	4.64	7.31 †	9.13	24.9

TABLE V

TITRATION OF Pb^{+2}-Tl^{+} MIXTURE WITH $KMnO_4$ IN PRESENCE OF TELLURIC ACID AND 0.1*N* NaOH

Max. inflec. per 0.1 ml in mV	*Vol. taken in ml*		*Theor. end-point in ml*		*Exper. end-point in ml*	*Error %*
	Pb^{+2}	*Tl^{+}*	*Pb^{+2}*	*Tl^{+}*		
$KMnO_4$ = 0.1204*N*, Pb^{+2} = 0.1202*N*, Tl^{+} = 0.0517*N*:						
49	5	5	8.32	3.58	12.37	—7
$KMnO_4$ = 0.1438*N*, Pb^{+2} precipitated as sulphate, NaCl catalyst:						
108	10	10	13.93	5.99	5.97	—0.33
124	5	25	6.97	14.98	14.92	—0.34
$KMnO_4$ = 0.02876*N*, Pb^{+2} precipitated as sulphate, NaCl catalyst:						
71	10	5	69.65	14.98	14.95	—0.21
62	5	2	34.85	5.99	5.97	—0.33
$KMnO_4$ = 0.01438*N*, Pb^{+2} ppt. as $PbSO_4$, Pb^{+2} = 0.1202*N*, Tl^{+} = 0.01262*N*:						
72	10	5	7.31	7.31	7.45	1.92
32	10	5	7.31	7.31	7.39	1.1
$KMnO_4$ = 0.002876*N*, Tl^{+} = 0.001262*N*, Pb^{+2} pptd as sulphate:						
12	10	5	69.55	3.65	5.8	58.9

II. *Reduction of $KMnO_4$ with Pb^{+2}-Tl^{+} mixture*

Undoubtedly a mixture of Pb^{+2} and Tl^{+} when used in titrating $KMnO_4$, will bring about its reduction and the volume taken will be the calculated value (*cf.* Fig. 3 A). This is apparent from the following results obtained by titrating $KMnO_4$ in 1*N* NaOH and in presence of Ba^{+2} ions:

Reduction of 100 ml 0.1436*N* $KMnO_4$ with Tl^{+}-Pb^{+2} mixture, Pb^{+2} = 0.01202*N*, Tl^{+} = 0.01262*N*.

Max. inflec.	*Theor. end-point*	*Exper. end-point*	*Error %*
64 mV	11.67 ml	11.63 ml	0.34
88 mV	,, ,,	11.64 ml	0.26

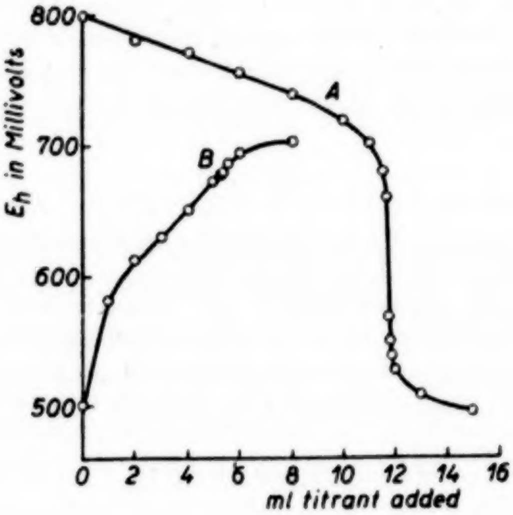

Fig. 3. (A) Titration of 10 ml 0.1438*N* $KMnO_4$ in 1*N* NaOH + Ba^{+2} ions with a mixture of Tl^{+} = 0.01262 and Pb^{+2} = 0.01202.
(B) Titration of $PbSO_4$ dissolved in ammonium acetate with 0.1294*N* $KMnO_4$ (= 10 ml 0.1202*N* Pb^{+2}).

TABLE VI

$KMnO_4$ = 0.01204*N*, Tl^{+} = 0.00368*N*, Pb^{+2} = 0.1202*N*

Alkalinity	*Max. inflec. per 0.1 ml $KMnO_4$*	*Vol. taken*		*Theor. end-point for Tl^{+}*	*Exp. end-point*	*Error %*
		Pb^{+2}	*Tl^{+}*			
Lead precipitated once:						
0.1*N*	32 mV	50 ml	10 ml	4.74 ml	4.59 ml	3.16
0.1*N*	37 ,,	25 ,,	10 ,,	4.74 ,,	4.67 ,,	1.48
0.1*N*	27 ,,	10 ,,	10 ,,	4.74 ,,	4.70 ,,	—0.84
Lead precipitated twice:						
0.1*N*	38 mV	25 ml	10 ml	4.74 ml	4.73 ml	—0.21
0.1*N*	44 ,,	10 ,,	10 ,,	4.74 ,,	4.76 ,,	0.42

III. *Estimation of* Tl^+ *after precipitating* Pb^{+2} *as* $PbSO_4$ *and filtering off the precipitate*

The interference of Pb^{+2} in the determination of Tl^+ can be completely eliminated by filtering off the $PbSO_4$ precipitate. In the filterate Tl^+ is determined with $KMnO_4$ after neutralizing the acid and making the solution 0.1*N* with respect to NaOH. The results obtained are low owing to the co-precipitation of part of Tl^+ with the $PbSO_4$ precipitate. By dissolving $PbSO_4$ in ammonium acetate, reprecipitating it and titrating the combined filtrate from both precipitations, better results are obtained (*cf.* Table VI).

Trials to titrate the lead after dissolving the $PbSO_4$ precipitate in ammonium acetate did not yield any result. Reduction of $KMnO_4$ passed partially to manganate without the appearance of an end-point (see curve B, Fig. 3).

SUMMARY

Pb^{+2} ($\sim$ 37-0.6 mg) and Tl^+ (45-0.9 mg) can be estimated by mixing with $KMnO_4$ in presence of Ba^{+2} ions and 1*N* NaOH. The excess $KMnO_4$ is then titrated with formic acid.

A mixture of Pb^{+2} and Tl^+ is oxidized simultaneously with $KMnO_4$ in 0.1*N* NaOH. Pb^{+2} interferes also when precipitated as sulphate or tellurate. In presence of SO_4^{-2} and telluric acid, thallium can be titrated only when its concentration is not less than 30 mg, below which lead seriously interferes. Tl^+ can be accurately determined in the filtrate from the $PbSO_4$ precipitate.

RÉSUMÉ

Pb^{+2} ($\sim$ 37-0.6 mg) et Tl^+ (45-0.9 mg) peuvent être dosés par addition de permanganate, en présence d'ions Ba^{+2} et de NaOH 1*N*. L'excès de $KMnO_4$ est ensuite titré par l'acide formique. Le mélange Pb^{+2} et Tl^+ est oxydé simultanément par $KMnO_4$ dans NaOH 0.1*N*. Pb^{+2}, précipité comme sulfate ou tellurate, gêne. En présence d'ions sulfuriques et telluriques le thallium peut être titré seul lorsqu'il se trouve en quantité supérieure à 30 mg; au-dessous de cette quantité, Pb^{+2} gène considérablement. Tl^+ peut être dosé avec précision après filtration de $PbSO_4$ précipité.

ZUSAMMENFASSUNG

Man kann Pb^{+2} (zwischen 37 und 0.6 mg) oder Tl^+ (zwischen 45 und 0.9 mg) durch Mischung mit $KMnO_4$ in Anwesenheit von Ba^{+2} Ionen und 1*N* NaOH bestimmen. Der Überschuss an $KMnO_4$ wird dann mit Ameisensäure titriert.

Eine Mischung von Pb^{+2} und Tl^+ wird gleichzeitig mit $KMnO_4$ in 0.1*N* NaOH Lösung oxydiert. Pb^{+2} stört auch wenn es als Sulfat oder Tellurat ausgefällt ist. Tl^+ kann nur in Anwesenheit von SO_4^{-2} und Tellursäure titriert werden, wenn seine Konzentration nicht geringer als 30 mg ist, da sonst das Blei stört. Tl^+ kann im Filtrat nach der Abscheidung von $PbSO_4$ genau bestimmt werden.

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THE DETERMINATION OF COPPER IN WHETLERIZED CARBON FOLLOWING DESTRUCTIVE OXIDATION OF CARBON EMPLOYING HOT CONCENTRATED PERCHLORIC ACID

by

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INTRODUCTION

Whetlerized carbon is granular adsorbent carbon used in gas mask canisters. Whetlerization involves the incorporation of appreciable amounts of copper to serve as catalyst enhancing its absorption efficiency. The copper content generally covers the range from 5 to 12 %.

Dry combustion of samples of whetlerized carbon has been proposed as a preliminary step with determination of copper in the ash thus obtained. This recovery of copper is attained at the expense of ignition equipment, a necessity for the dissolution of the ash and resultant determination of copper in a number of well known procedures.

The present method, (employing "the liquid fire reaction")[1,2,3], is designed to destroy the carbon by the use of boiling mixed $HNO_3 + HClO_4 + H_2SO_4$, with a small amount of chromium to serve as catalyst and retain the copper. The copper residuum as soluble ashed product is boiled to expel the nitric acid and partially volatilize the perchloric acid. The copper is then determined iodimetrically. The method is rapid and precise and accompanied by no hazard. The chromium catalyst is easily removed from the oxidized sample by the process of its removal as chromyl chloride, CrO_2Cl_2, and thus does not interfere. Chromium also does not interfere if reduced to Cr(III) by addition of hydrochloric acid to the hot sulfuric acid solution of the wet ashed sample.

Previously described liquid fire reactions

The wet oxidation of coal and of coke in preparation of such samples for the determination of sulfur has been described by SMITH AND DEEM[4], and their procedure has been widely adopted in routine control industrial operations. Carbon and other carbon compounds in coal are not rapidly oxidized by boiling with concentrated perchloric acid. Some samples require 60 to 180 minutes treatment. By the use of chromium as catalyst the time of digestion is reduced to as low as 15 minutes and less, if a little vanadium is used as catalyst. Granular gas mask carbon is quite equal in resistance to wet oxidation as to compare with the wet oxidation of coke. For this reason the most powerful oxidation medium is employed consisting of $HNO_3 + HClO_4 + H_2SO_4$, with added chromium as catalyst. The completion of the destruction of the last trace of organic matter is indicated by the subsequent oxidation of Cr(III) to CrO_3 shown by the color change from green to orange.

The mixed acids upon boiling, operate through the destruction of the most easily oxidized positions of the sample at 140-150 degrees. The excess nitric acid is then volatilized and at 150-160 degrees the hot concentrated perchloric acid continues the oxidation and begins to volatilize at 160 degrees. It may be completely removed by heating the mixed $HClO_4 + H_2SO_4$ to a temperature of 195-200 degrees. During this rise in temperature from 160 degrees to 200 degrees the oxidation potential of the hot concentrated $HClO_4$ gradually and relentlessly augments until practically all organic matter has been oxidized. If any small amount of organic matter remains at this point, further heating increases the residual $HClO_4$ concentration from 70% to 85% at some temperature close to 180-190° C and no known organic matter can withstand oxidation at the high oxidation potential thus attained.

The oxidation potential of the acid mixture gradually ascends from 1 to 2 volts or better, stepwise, during the digestion period and all organic matter is consumed and converted to CO_2 smoothly and rapidly. Finally the solution changes from green to orange and the wet combustion is complete.

Apparatus employed

This has previously been described in detail[1] and needs little further description here. Employ vycor reaction flasks (conical 500 ml), a refluxing still head to avoid loss by spray formation, and an electric hot plate as the source of heat. The removal of fumes without the use of a fume hood is provided for by employment of a fume eradicator,[1] and water aspirator pump.

Reagents

a. Nitric acid (Sp. Gr. 1.42)
b. Perchloric acid 70-72% (Sp. Gr. 1.67-1.68)
c. Sulfuric acid 95% (Sp. Gr. 1.84-1.85)
d. Potassium dichromate, ($K_2Cr_2O_7$)
e. Hydrochloric acid 37% (Sp. Gr. 1.12)
f. Standard 0.1*N* $Na_2S_2O_3$, glacial acetic acid and amylose starch paste indicator
g. 50% NaOH solution and dilute approx. (0.5*N* NaOH solution)
h. KI crystals

OPERATION PROCEDURE

Preparation of sample. The sample must be ground to pass completely through a 40 mesh seive. It was found by test that 60% of the sample thus ground passed through a 60 mesh seive. An even finer grade sample would be preferred but is not a requirement. Moisture contamination during rapid grinding is negligible.

Digestion operation. An accurately weighed 1.0 to 2.0 gram sample is transferred to a 500 ml conical vycor flask, (pyrex flasks or the equivalent may be used but are not nearly as suitable). Add 10 ml of concentrated sulfuric acid, 5 ml of 70-72% perchloric acid and 10 ml of concentrated nitric acid. Add approximately 25-50 mg of potassium dichromate to serve as catalyst. The order in which the reagents are added is immaterial. Place a refluxing still head and fume eradicator in position, (as in Fig. 3, page 411, reference [1]) with a brisk flow of air through the fume scrubber bottle connected to the water jet aspirator pump. The first period of digestion should be carried out at a temperature just sufficient to boil the reaction mixture, but not rapidly boil off the low-boiling nitric acid. The nitric acid reaction is complete when brown fumes are no longer evolved. Raise the temperature to an extent capable of producing a final temperature of 190-200 degrees and continue the digestion. The perchloric acid should fume strongly but not reflux more than three-fourths of the way to the top inside walls of the digestion flask. When all organic matter is destroyed the solution of the ashed sample will turn orange from the oxidation of Cr(III) to CrO_3.

Removal of chromic acid catalyst. When all the carbon is oxidized, (after the solution has turned orange a few black specks may remain which are not carbon and carry no copper), the temperature is raised until the $HClO_4$ is volatilized. Now add hydrochloric acid dropwise, at 5-10 second intervals through the dropping funnel of the fume eradicator apparatus. The chromium is thus volatilized as CrO_2Cl_2. If all perchloric acid has been evolved the addition of the hydrochloric acid will reduce the Cr(VI) to Cr(III) which gives the solution a green color and does not interfere with subsequent operations. All chromium must be reduced or volatilized to prevent interference in the iodimetric determination of copper which follows.

Preparation of the solution for determination of copper. Remove the flask and contents from the hot-plate and cool it by immersion in an ice and water bath employing a swirling motion. The use of sections of rubber tubing as thumb and index finger caps, (a 40 mm length of heavy wall rubber tubing, of 2 mm wall thickness), is adequate. Immerse the protected fingers in the water bath to prevent their sticking to the hot outside walls of the neck of the flask. When the flask contents are cool, add 50 ml of distilled water, and again cool the contents of the flask. Remove and rinse the refluxing still head and neutralize the greater portion of the sulfuric acid by the addition of strong caustic soda solution. Now add dilute caustic soda solution until the blue copper hydroxide just fails to re-dissolve.

Add 5 ml of diluted glacial acetic acid, (1 vol acid + 3 volumes of water) and cool the resulting solution. Dilute to 150 ml with distilled water and add 4-5 g of potassium iodide crystals. Swirl the solution for a minute or more to complete the liberation of iodine. Titrate the iodine liberated by the addition of 0.1*N* sodium thiosulfate until almost all iodine has reacted. Add a fragment of amylose starch paste and complete the titration of iodine to the disappearance of the starch-iodine blue color. The reactions involved are:

$2\,Cu^{+2} + 4\,I^- = 2\,CuI\ (\text{insoluble}) + I_2$

$I_2 + 2\,S_2O_3^{-2} = S_4O_6^{-2} + 2\,I^-$

The results by multiple test. These are shown in Tables I, II, and III.

TABLE I

THE DETERMINATION OF COPPER IN WHETLERIZED CARBON WITHOUT FURTHER SUBDIVISION

Sample taken = 1 gram

Analysis No.	*0.09932N $Na_2S_2O_3$ ml*	*Cu found mg*	*Cu percent*	*Error from average*
1	19.85	125.2	12.52	+0.43
2	18.90	119.3	11.93	—0.16
3	19.15	120.9	12.04	—0.05
4	18.80	118.7	11.87	—0.22
			Av. 12.09	

The conclusion as indicated from the results shown in Table I is that the sample is not of uniform composition. This conclusion is justified by the results given in Table II on another sample of whetlerized carbon.

TABLE II

THE DETERMINATION OF COPPER IN WHETLERIZED CARBON

Samples ground to pass 40 mesh seives

Sample Wt g	*0.09932N $Na_2S_2O_3$ ml*	*Copper found mg*	*Copper found %*	*Error from average in %*
	7.71	48.6	4.80	+0.02
1	7.60	48.0	4.80	—0.04
1	7.78	49.1	4.91	+0.07
1	7.61	48.1	4.81	—0.03
2	15.40	97.2	4.86	+0.02
2	14.48	91.4	4.56	—0.28
2	15.37	97.0	4.85	+0.01
2	15.39	97.1	4.86	+0.02
2	15.47	97.6	4.88	+0.04
2	15.29	96.5	4.88	+0.04
2	15.72	99.3	4.97	+0.13
2	15.20	96.0	4.80	—0.04
2	15.43	97.5	4.88	+0.04
2	15.10	95.3	4.77	—0.07
	0.0	0.0	Av. 4.84	Av. 0.03

References p. 119

A standard sample of whetlerized carbon was not available. The accuracy with which copper is determined following the described procedure, was determined by the reanalysis of the same sample as that employed in the case of Table II, after the addition of known weights of copper metal to each sample and before destructive oxidation of the organic matter by the liquid fire reaction. The data are given in Table III.

TABLE III

THE DETERMINATION OF ADDED COPPER IN THE WET OXIDATION OF WHETLERIZED CARBON

Sample taken-2 grams
Copper added as metal shot

Sample No.	*Cu added g*	*0.09932N $Na_2S_2O_3$ req'd. ml*	*0.09932N $Na_2S_2O_3$ req'd. for added copper ml*	*Added copper found g*	*Error in copper g*
1	0.1509	39.38	24.02	0.1519	+0.0010
2	0.1500	39.19	23.83	0.1506	+0.0006
3	0.1522	39.31	23.95	0.1512	+0.0012
4	0.1535	39.80	24.44	0.1544	+0.0009
5	0.1535	39.40	24.04	0.1518	+0.0017
				Av.	+0.0011

From an examination of the data in Table III it will be observed that the procedure as described can be claimed to give results with 0.1% of the true values.

General procedural appraisal. The method as described requires 25-30 minutes for the completion of a single analysis using the equipment designated for individual analysis. The method is well adapted to multiple simultaneous determinations if a large hot-plate and good fume hood is provided to carry away evolved gases from the digestion sample flasks.

The use of vycor digestion flasks is strongly recommended although pyrex or equivalent type glass reaction flasks may be employed. The chilling, by immersion, of flasks containing hot concentrated sulfuric acid using vycor ware may be performed without caution in such equipment. The use of pyrex ware or its equivalent demands more cautious treatment which is time-consuming and inconvenient.

The use of rubber finger protection as described to facilitate the rapid handling of hot reaction flasks, (reference 5, Fig. 21, page 37) greatly facilitates operative manipulations. The tendency for such rubber finger caps to stick to hot surfaces is eliminated if the rubber is wetted by immersion, momentarily, prior to use in grasping a hot reaction beaker or flask.

The use of the refluxing still head as described, together with the fume eradicator and water aspirator and scrubber, is a most convenient apparatus assembly for individual analyses without a required fume hood otherwise essential. The fume eradicator is conveniently removed at the completion of a reaction of digestion and may be set aside conveniently for subsequent flask manipulations of cooling and reagent addition without removal of the refluxing still head. For multiple digestions in a forced draft, fume hood flasks equipped with spray retention refluxing still heads only need be employed.

During hundreds of analyses employing this method no violent reactions were involved. If a protective screen is thought to be advisable it may of course be employed.

Operators soon dispense with its use in routine digestions as an unnecessary precaution.

In common with all methods employing the "liquid fire reaction"[1,2,3], the preparation of comparatively large samples of organic matter for the determination of either trace element metals or macro adulterations, the wet ashing procedure is a profitable economy accompanied by major conservation of time and apparatus simplification.

SUMMARY

The determination of copper in whetlerized gas mask carbon has been described. The sample is "ashed" by wet oxidation employing mixed $HNO_3 + HClO_4 + H_2SO_4$. The reaction is catalyzed through the addition of small amounts of chromium.

The copper recovered as copper sulfate following wet ashing is reduced to Cu(I) by potassium iodide in acetic acid solution (with previous neutralization of sulfuric acid by sodium hydroxide). The liberated iodine is then titrated employing standard sodium thiosulfate solution with starch as indicator.

Individual analyses require 25-30 minutes for complete analysis.

RÉSUMÉ

Une méthode est décrite pour le dosage du cuivre dans le carbone „whetlerisé" des masques à gaz. La substance à analyser est minéralisée par attaque au moyen d'un mélange $HNO_3 + HClO_4 + H_2SO_4$. La réaction est catalysée par addition de faibles quantités de chrome. Le cuivre, après la minéralisation se trouve sous forme de sulfate; il est réduit en cuivre (I) par l'iodure de potassium en solution acétique (après neutralisation de l'acide sulfurique par l'hydroxyde de sodium). L'iode libéré est ensuite titré par une solution étalon de thiosulfate de sodium en présence d'amidon comme indicateur. Une analyse complète demande 25 à 30 minutes.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben, um Kupfer in der „whetlerisierten" Kohle von Gasmasken zu bestimmen. Die zu analysierende Substanz wird mineralisiert mit einem Gemisch von $HNO_3 + HClO_4 + H_2SO_4$. Die Reaktion wird katalysiert durch eine Zugabe von kleinen Mengen Chrom. Nach der Mineralisation ist das Kupfer in Form von Sulfat vorhanden; es wird mit Kaliumiodid in einer essigsauren Lösung zu Kupfer(I) reduziert (die Schwefelsäure wird dabei mit Natronlauge neutralisiert). Das freie Jod wird darauf mit einer Vergleichslösung von Natriumthiosulfat, in Anwesenheit von Stärke als Indikator, titriert. Für eine vollständige Analyse braucht man 25 bis 30 Minuten.

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DIRECT TITRATION OF CARBON DIOXIDE

by

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INTRODUCTION

The determination of carbon dioxide is one of the most common of the analyst's tasks and therefore a great number of papers, some in the last decade, have been published on this subject. The most important of these deal with determination of CO_2:

1. In air or other gases (*e.g.* measurements of combustion rates)[1-7].
2. In water[8-10].
3. In dry-combustion products (carbon in steel, determination of carbon and oxygen in organic substances)[11].
4. In wet-combustion products (determination of organic matter by chromic-acid oxidation)[12].
5. In products formed in decarboxylation experiments[13].
6. In products formed in physiological experiments (investigations involving carbon metabolism in aerobic fermentations *etc.*)[14,15].

For the greater part, these methods are based on a relatively small number of principally different procedures, which are:

(a) Indirect acidimetric. CO_2 is absorbed in alkaline solution ($Ba(OH)_2$, KOH) and the excess of alkali is titrated back.

(b) Gravimetric. CO_2 is absorbed on soda-asbestos on sodalime or in alkaline solution and the increase in weight is determined.

(c) Volumetric. CO_2 is absorbed in alkaline solution and the decrease in volume is measured.

In addition, several methods for special purposes have been developed, *e.g.* those suitable for the continuous determination of CO_2 in a gas stream. The most important thereof are based on measurements of changes in:

(d) The conductivity of an alkaline solution owing to CO_2 absorption.

(e) The infra-red absorption-capacity of a gas.

(f) The colour-intensity of an alkaline indicator solution owing to absorption of carbon dioxide.

Depending on the kind of problem he has to solve, the analyst will choose one of these methods. However, all of them have special disadvantages in one or more of the following respects:

(1) the procedure takes up much time (a, b),

(2) it is only suitable for relatively large quantities (c),

(3) the method is expensive owing to the need of a complicated apparatus, especially if a high degree of accuracy is required (d, e, f),

(4) the method is indirect and therefore unsuitable for continuous measurements (a, b, c).

In searching for a simple method of estimating the components of a mixture separated on a gas-liquid partition column, we succeeded in finding a procedure for direct titration of the CO_2 formed by oxidation of these components over copper oxide. With this method the disadvantages mentioned above are avoided, it being rapid, adaptable to samples of almost any concentration, inexpensive and highly accurate. However, it will be difficult to develop an automatic recorder operating on this principle.

It is a well known fact that various organic liquids are more suitable for collection of CO_2 than are the aqueous solutions of hydroxides. PARKES *et al.*[16] state that dipiperidyl absorbs CO_2 about ten times more rapidly than do the aqueous absorbents. Other absorbents recommended in the literature are: ethanolamine[17] and ethylenediamine[18], used mainly for industrial purposes. In these solvents the CO_2 is not only dissolved but also chemically bound. The use of organic solvents only for raising the solubility of CO_2 was suggested by VAN NIEUWENBURG[19], who used a mixture of aniline, ethyl alcohol and barium hydroxide to collect the carbon dioxide. In our method, use is made of the relatively great solubility of CO_2 in pyridine or acetone, which enables us to titrate the CO_2 absorbed from a gas stream directly with a sodium methylate solution.

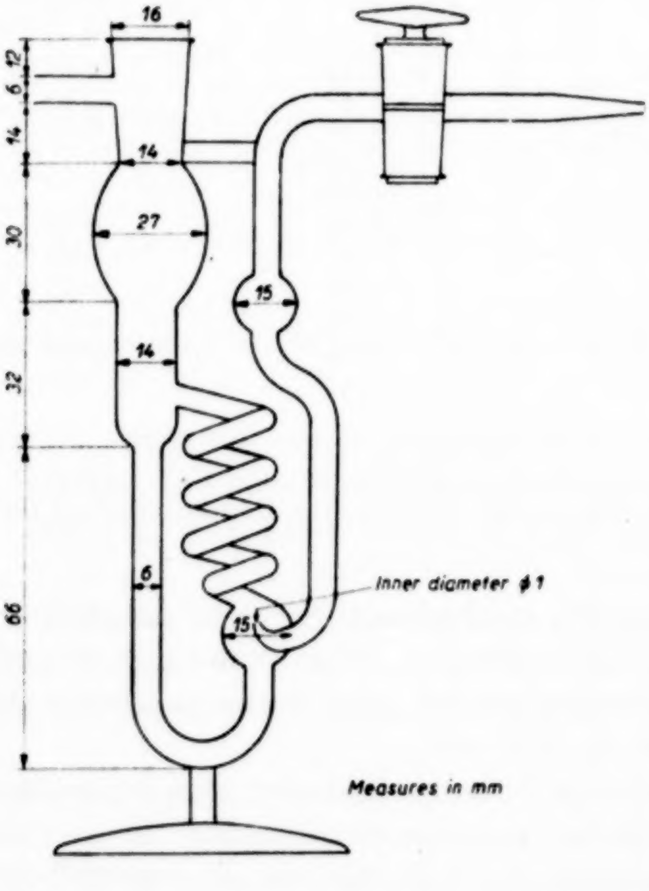

Fig. 1

EXPERIMENTAL

The apparatus used is shown in Figure 1. The absorption-vessel, which is identical with that used by PIETERS[20], is easy to construct. It is designed for circulation of the pyridine on the principle of an air lift. The dimensions may be varied over a wide range, depending on the CO_2 concentration or the amount of CO_2 to be measured. However, for many purposes the apparatus as shown here will do.

Three kinds of determinations were performed.

1. *Determination of carbon dioxide in air*

Air from the compressed-air line was conducted through a tower filled with anhydrone, and then through a flow meter connected to the titration vessel. A second vessel was used for checking the CO_2 absorption in the first. A number of experiments were performed at different flow rates. The results are listed in Table I. In all experiments the flow time was exactly 15 minutes.

TABLE I

DETERMINATION OF CARBON DIOXIDE IN AIR

Solvent: pyridine Air sample I	*Flow rate l per hour*	*ml titrant (0.0110N $NaOCH_3$) used in vessels I + II*	*ml titrant used in vessel II*	*CO_2 found vol. %*
	1.0	0.36	0.00	0.038
		0.39	0.00	0.041
	2.1	0.77	0.00	0.039
		0.78	0.00	0.039
	3.2	1.17	0.03*	0.039
		1.17	0.07*	0.039
	4.0	1.54	0.08*	0.041
		1.48	0.04	0.039
	5.0	1.76	0.05	0.038
Solvent: acetone Air sample II		*(0.00995N $NaOCH_3$)*		
	1.0	0.39	0.00	0.037
	3.0	1.19	0.05	0.038
	4.9	1.83	0.02	0.036
	6.9	2.65	0.03	0.037
	9.0	3.29	0.08	0.035
	9.0	3.28	0.09	0.035

* These experiments were carried out with a titration fluid containing the titrant added in the foregoing experiments. For the second 4 l experiment fresh titration fluid was used.

The results prove that the method enables us to determine the CO_2 content of air with an accuracy of ± 0.001% absolute within 15 minutes. If a higher degree of accuracy is desired, special attention has to be paid to several important factors:

(a) the measurement of the flow rate,

(b) the solvent for the titrant; methyl alcohol can be replaced by methyl alcohol-pyridine mixtures, giving a sharper end-point,

(c) the accuracy of the buret reading; the use of a micro-buret might be preferable.

The authors are convinced that it must be possible to attain almost the same precision as reached by SPECTOR AND DODGE[4] with their colorimetric method, with experiments lasting about half an hour.

However, the volume of air needed is three times as large as that needed for the colorimetric procedure.

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In order to find out the maximum flow rate for a desired precision of ± 0.001 vol. % CO_2 in air (with pyridine as a solvent) without the necessity of a titration in the second vessel, a number of tests were run with flow rates of successively 6, 7, 8, 9 and 10 l per hour. There was a steady increase in the quantity of CO_2 slipping through, which, at a flow rate of 10 l per hour, amounted to about 0.15 ml of titrant, *i.e.* about 0.002 vol. % CO_2 absolute; with acetone as a solvent this effect is somewhat smaller (see Table I). With the apparatus used, it is not advisable to increase the flow rate much beyond 10 l per hour without titration in the second vessel.

Besides pyridine, also picoline bases, aniline, dioxane and cyclohexanone were tested for usefulness. The picoline bases are discussed below.

A test with aniline demonstrated that at a flow rate of 4 l per hour more than 25% of the CO_2 is contained in the second absorption vessel. Moreover, it was evident that part of the CO_2 had been lost, the CO_2 content of a sample of air appearing to be 0.035% with pyridine and 0.029% with aniline as a solvent.

Dioxane and cyclohexanone are also less convenient, both catching but 85% of the CO_2 in the first vessel.

Procedure of the CO_2 determination in gases

Place two circulation vessels (see Fig. 1) in series; close the cocks of these vessels; fill both vessels with acetone to half their capacity and add a small quantity of thymol blue.

Fit the microburets hermetically on the vessels. Connect the gas stream to the vessels, open the cocks and adjust the velocity.

Neutralize the solution in the first vessel, add a small excess amount of CH_3ONa solution and then neutralize the solution in the second vessel accurately. Take care that during the neutralization of the solution in the second vessel there is always a small excess of CH_3ONa solution in the first.

Press the stopwatch at the first change of colour in the first vessel and note the buret readings.

Keep neutralizing the dissolved CO_2.

On concluding the experiment take down the buret readings and note the time. Read the flow rate of the gas on the flow meter. With these data, the % of CO_2 in the gas can be calculated.

2. *Determination of semi-micro and micro quantities of carbon dioxide in combustion products*

Owing to the need of a method for direct titration of CO_2 formed by combustion of the components of a mixture, separated on a gas-liquid partition column, a number of tests were run (see Table II). Weighed amounts of pure organic compounds (equivalent to definite amounts of CO_2), were combusted in a silica tube filled with copper oxide (800 °C), and the CO_2 formed was transported by a stream of air to an absorption vessel filled with pyridine.

The flow rate of the air was about 3 l per hour, the maximum rate used in the separation experiments.

The titration was performed as described above, the titrant being (0.1*N*, 0.01*N* or 0.02*N*) sodium methanolate in methanol. A few tests were run with $CaCO_3$ which was heated slowly to 900° C for complete decomposition. However, it proved to be rather difficult to get accurate results with this procedure, probably because of the frequent occurrence of high CO_2 concentrations in the gas leaving the combustion tube.

For experiments in which a maximum relative error of about 1% was allowed, this procedure was satisfactory. The titrant was standardized against benzoic acid in pyridine as a solvent.

TABLE II

DETERMINATION OF CO_2 OBTAINED IN THE COMBUSTION OF ORGANIC COMPOUNDS

Compound used	*Normality strength of titrant*	*CO_2 present mg*	*CO_2 found mg*	*Error mg*
Benzoic acid	0.1N	12.9	13.0	+0.1
		18.9	18.7	−0.2
		26.8	26.7	−0.1
Succinic acid	0.1N	14.8	14.7	−0.1
		19.3	19.0	−0.3
		19.7	19.7	0.0
		24.5	24.4	−0.1
Saccharose	0.1N	9.0	9.1	+0.1
		14.7	14.8	+0.1
		20.1	19.8	−0.3
		19.0	19.0	0.0
Succinic acid	0.02N	3.51	3.55	+0.04
		2.68	2.69	+0.01
		3.26	3.24	−0.02
		3.68	3.68	0.00
Calcium carbonate (dec.^{n})	0.02N	5.83	5.81	−0.02
	0.01N	2.87	2.86	−0.01

3. *Adaptation of the method to micro and semi-micro elementary analysis* (carbon and oxygen determination)

From the results mentioned above we concluded that it might be possible to find a more accurate procedure by taking special precautions.

The factors which had to be considered were:

(a) the sharpness of the end-point determination,
(b) the standardization of the titrant,
(c) the blank value (*e.g.* CO_2 content of the transport gas),
(d) the accuracy of the buret reading,
(e) the loss of CO_2 owing to incomplete absorption.

(a) As was reported above, the sharpness of the colour change at the end of the titration was unfavourably affected by the addition of methanol from the titrant. A titrant made up of CH_3ONa dissolved in a mixture of methanol-pyridine (1 : 4) proved to be very satisfactory for micro-analysis. For semi-micro work this titrant gave difficulties owing to the small solubility of sodium bicarbonate in the solvent mixture. Therefore the use of pyridine in the methanolate solution has no advantage in this case.

(b) The standardization of the titrant against benzoic acid left much to be desired, especially because of the small solubility of sodium benzoate in the solvent mixtures. Precipitation of this product causes a poor end-point. Standardization against known amounts of CO_2 gave much better results.

(c) With special precautions the blank value could be diminished to about 0.002 ml

0.02*N* sodium methylate per minute. This value was still somewhat variable, so that it had to be determined frequently. The time needed for an experiment was noted and the blank value calculated. For semi-micro work the blank value is negligible.

(d) A buret with a total volume of 10 ml was used. Therefore it was necessary that the precision of the buret reading should amount to ± 0.01 ml. In most cases the sharpness of the end-point was such that 0.01 ml titrant gave a well-perceptible colour change.

(e) Especially in micro-analysis (titrant 0.02*N*) loss of carbon dioxide owing to incomplete absorption may occur if insufficient care is taken. The most important precaution to avoid this is to prevent the absorbent solution from turning wholly yellow during analysis. (A local yellowness is of no consequence.) Further, as reported above, the concentration of the CO_2 in the absorbed gas may not be too high. In the common carbon and oxygen determination *via* CO_2 this difficulty is not to be expected. Anyhow, it is advisable to connect to the titration vessel a second smaller one as a control means. Eventually, traces of CO_2 absorbed therein can also be titrated.

The results obtained with this accurate procedure are shown in Table III.

TABLE III

MICRO-DETERMINATION OF CARBON IN ORGANIC COMPOUNDS*

Compound used	*Sample weight mg*	*% C calc.*	*% C found*	*Error % abs.*
Succinic acid	3.148	40.68	40.66	—0.02
	2.663		40.88	+0.20
Saccharose	2.092	42.10	42.37	+0.27
	2.623		42.02	—0.08
	1.828		41.97	—0.13
	2.561		42.13	+0.03
	2.614		41.45**	—0.65
	2.579		41.92	—0.18
	4.691		42.08	—0.02
Benzoic acid	1.987	68.84	68.57	—0.27
	2.733		69.00	+0.16
	2.529		69.05	+0.21
Hydrochinone	2.539	65.44	65.24	—0.20
	2.757		65.14	—0.30
Maleic acid	2.375	41.39	41.41	+0.02
	3.256		41.13	—0.26
	3.010		41.65	+0.24

* These experiments were run in a very simple provisional combustion apparatus.

** In this case the combustion took place in a few minutes, giving rise to an instantaneous high concentration of CO_2.

The normality of the sodium methylate solution was estimated in the same way, *viz.*, by combustion of a known amount of benzoic acid and titration of the CO_2 formed.

The 0.02*N* sodium methylate solution was prepared by dilution of a pipetted amount of 0.1*N* sodium methylate in methylalcohol with pyridine. Both titrants mentioned in Table IV were made from the same 0.1*N* solution, B a week after A; it is seen from the results that the reproducibility of this procedure is very good and that the 0.1*N* solution is very stable.

TABLE IV

STANDARDIZATION OF THE TITRANT AGAINST CO_2 OBTAINED IN THE COMBUSTION OF BENZOIC ACID

Titrant solution	*Benzoic acid mg*	*Titrant used ml*	*Normality calc.*	*Mean value*
A	2.107	6.44	0.01875	0.01873
	2.766	8.49	0.01867	
	2.432	7.43	0.01876	
	2.346	7.17	0.01875	
B	2.153	6.61	0.01867	0.01874
	2.709	8.28	0.01875	
	2.548	7.76	0.01882	
	2.286	7.00	0.01872	

The standardization was also tried with $CaCO_3$ (decomposition at 900° C), which has a much higher equivalent weight, but the results varied more than those mentioned above (max. $\pm$ 0.00018), it being more difficult to prevent the formation of high CO_2 concentrations in the absorbed gas.

Besides pyridine, a mixture of picoline bases was also tried as a solvent for the CO_2 and as a medium for titration. We did not succeed in getting reliable results, most probably because of the formation of some Na_2CO_3 instead of $NaHCO_3$.

DISCUSSION

In our opinion an essential condition of the possibility of direct CO_2 titration is a relatively high solubility of the CO_2 in the solvent used. According to JUST[21] and KUNERTH[22] the solubility in pyridine in cc gas per cc solvent at 20° C (S_{20}) is 3.86, the solubility in water being 0.85 cc[23]. Other solvents studied by JUST and comparable with pyridine are, *e.g.* Methanol: $S_{20} = 4.20$, methyl acetate: $S_{25} = 6.49$, *iso*butyl acetate: $S_{20} = 4.97$ and many other esters, acetic anhydride: $S_{20} = 5.7$, ethylene chloride: $S_{20} = 3.80$, di-ethyl ether: $S_{15} = 5.18$[24] and acetone $S_{20} = 6.92$.

A much lower solubility is found for benzene: $S_{20} = 2.54$, nitrobenzene: $S_{20} = 2.66$, aniline: $S_{20} = 1.43$ and toluidine: $S_{20} = 1.47$.

The low value for aniline is in accordance with our observations.

However, there is another condition of the applicability of a solvent: the titration end-point has to be sharp. As was said before, methanol causes a poor end-point. This was also observed with di-ethyl ether and ethylcellosolve. Esters and anhydrides tend to saponify. Ethylene chloride and the like have the disadvantage of being very poor solvents for sodium bicarbonate.

Only acetone provides an end-point comparable with that in pyridine. Over this solvent, acetone has several advantages: (1) it is a better solvent for CO_2, (2) it is much cheaper than pyridine, (3) it has no unpleasant smell. However, it has the disadvantage of being more inflammable. The applicability of acetone will be subjected to a further study.

APPLICATION

From the results reported above it will be clear that the proposed method may be widely applied to CO_2 determinations. Especially in those cases where direct measurement of the amount of CO_2 generated per time unit, is essential, the method will have many advantages, but the authors are convinced that for almost any of the purposes mentioned in the introduction, the method will be applicable. We intend to make use of the method in this laboratory for the following purposes:

(a) micro and semi-micro determination of carbon,
(b) micro and semi-micro determination of oxygen (conversion into CO_2 as described by DEINUM AND SCHOUTEN[25]),
(c) determination of carbon in steel,
(d) determination of CO_2 formed in wet-combustion processes.
(e) determination of CO_2 in air.

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SUMMARY

A brief survey is given of the most important methods for the determination of carbon dioxide, and the suitability of these methods is briefly discussed.

Details are given of a direct carbon dioxide titration method developed for the detection and determination of substances separated on a gas-liquid partition column. The titration is performed in pyridine or acetone as a solvent and with a sodium methylate solution as a titrant.

Results are given of determinations of carbon dioxide in air and, on semi-micro and micro scales, of carbon dioxide obtained by combustion of organic compounds.

It is suggested that the proposed method will be generally applicable, e.g.:
(1) to the micro and semi-micro determination of carbon and oxygen,
(2) to the determination of carbon dioxide formed in wet-combustion analysis,
(3) to the determination of carbon in steel.

RÉSUMÉ

Un compte rendu des plus importantes méthodes de dosage de l'anhydride carbonique est donné et les caractéristiques de ces méthodes sont brièvement discutées. Des détails sont donnés sur une méthode de titration directe de l'anhydride carbonique établie pour la détection et le dosage de substances séparées sur une colonne de partage gaz-liquide. La titration est effectuée dans la pyridine, ou dans l'acétone, comme solvant et au moyen de méthylate de sodium comme réactif. Des résultats sont donnés pour des dosages d'anhydride carbonique dans l'air et pour des dosages à l'échelle semi-micro et micro, d'anhydride carbonique obtenu par combustion de composés organiques.

On s'attend que la méthode signalée soit généralement applicable, par exemple:
(1) aux micro- et semi-microdosages de carbone et d'oxygène,
(2) au dosage d'anhydride carbonique formé par combustion par voie humide,
(3) au dosage du carbone dans les aciers.

ZUSAMMENFASSUNG

Es wird eine kurzgefasste Übersicht der wichtigsten Methoden zur Bestimmung des CO_2 gegeben und die Eignung dieser Methoden wird kurz besprochen. Es werden anschliessend Einzelheiten über eine Methode gegeben, die eine direkte Titrierung des CO_2 ermöglicht und zur Feststellung und Bestimmung von Substanzen entwickelt wurde, welche in einer Gas-Flüssigkeit-Verteilungskolonne getrennt wurden. Die Titration wurde in Pyridin oder Aceton als Lösungsmittel und mit einer Natriummethylatlösung als Titrierflüssigkeit durchgeführt.

Weiterhin werden die Resultate der Bestimmungen von CO_2 in Luft und der Mikro- und Halbmikrobestimmungen von durch Verbrennung organischer Verbindungen anfallendem CO_2 bekanntgegeben.

Angeregt wurde, dass die erwähnte Methode allgemeine Anwendung finden werde u.a.:
1. für Mikro- und Halbmikrobestimmungen von Kohlenstoff und Sauerstoff.
2. für die Bestimmung von CO_2, das durch Verbrennung auf nassem Wege gebildet wird.
3. für die Bestimmung von Kohlenstoff in Stahl.

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CHARACTERIZATION OF INKS BY PAPER CHROMATOGRAPHY, FOR CRIMINOLOGICAL PURPOSES

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The relatively small quantities of an ink that have been used for the writing of a given document make it almost impossible to analyse it chemically and very problematic to characterize it with common physical methods (ultraviolet and infrared rays, *etc.*). On the other hand, the research of the diffusion of the chloride and sulphate ions affords, as is well known, only indications as to the time when a given document has been written.

It is however well known that the problem, at least from a practical point of view, never presents itself as a chemical analysis, but rather as a simple comparative research on two or more types of ink on the same written text. It will therefore be sufficient, we believe, to find a comparative method that will enable one to reach a final decision as to whether the compared inks are or are not of the same type. Up to now several researches have been conducted on this matter and it appears that the problem will be solved successfully by adopting, as has been done especially in recent years, chromatographic methods. We note in this connection the works of ESPOSITO VITOLO[1] (capillary analysis on filter paper strips, in an oven at 100° and at room temperature) and VITOLO AND FORNARI[2] (adsorption on alumina as per Brockman).

Even before the publication of the above-mentioned works, we had undertaken the study of the comparative examination of various inks by means of the paper chromatography, and the present essay, which will be followed by further researches, covers precisely that subject.

We do not, in this essay, intend to present a systematic study of the various types of inks available today on the market, but we simply propose to set forth in which conditions it is possible to detect with the utmost precision the differences existing between various types of ink, in the quantities that are normally to be found in one or more letters or figures of a given document.

THEORETICAL PART

Since the time when chromatographic analysis was first adopted by TSWETT in 1906, it has found many applications in all the fields of chemistry and particularly in that of organic substances of a more or less complex constitution (carotenoids, vitamins, hormones, *etc.*). Its continuous success led, during the last ten years, to the development of new methods, such as that of paper chromatography in one or two dimensions and still more recently of circular paper chromatography[3].

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Actually, such an analysis had already been performed much earlier, in 1861, by SCHÖENBEIN in his study on capillary phenomena.

With paper chromatograms, the result of the examination is given by the R_F value, which expresses the relationship between the velocity of movement of the solute and the velocity of movement of the solvent. The R_F value depends mostly on the nature of the substance examined, *i.e.* on its molecular constitution.

In a chromatographic analysis one must allow for various factors that might influence the success of the chromatogram (temperature, pH, *etc.*) and one must choose with the utmost care not only the solvent in which the substance is dissolved, but also the developer, the reagents for the development of the various colourless zones, *etc.* A remarkable contribution has been afforded by ultraviolet light, especially for the examination of those substances that do not have a colour of their own and that cannot consequently be spotted in day light.

EXPERIMENTAL PART

1. *Inks examined.* (a) Carter's blue-black, (b) Carter's blue-rex, (c) Pelikan, (d) Parker Quink, washable blue, (e) Parker Quink, permanent blue, (f) Elvita, (g) Menounos, (h) Menounos, common. Elvita and Menounos are inks of Greek make.

2. *Dilution of the inks.* 0.1 ml of ink is diluted with 5 ml of an acid solution of ethyl alcohol, the solution being then ready for the chromatographic analysis.

The alcoholic solution is prepared by bringing 4 ml of conc. HCl to 100 ml with ethyl alcohol.

When the examined ink has to be extracted from one or more letters of a written document, the same acid solution of ethyl alcohol is used, while heat is used to facilitate the extraction.

3. *Choice of the quality of the paper.* Trials were carried out with various types of filter papers, produced by the German firm Carl Schleicher & Schüll (602h:P, 598G, 2040a, 2040b, 1101), and with various developers. For the normal rate of development and for regular progression of the circular zones (homocentric zones), type No. 1101 of paper was chosen.

4. *Developers.* The following were tried: (a) distilled water, (b) 5% solution of hydrochloric acid, (c) 80% ethyl alcohol, (d) alkaline solution of ethyl alcohol, (e) acid solution (HCl) of ethyl alcohol, (f) mixture of *n*-butanol and conc. acetic acid (1:1).

Of these, the best results were obtained with the butanol-acetic acid solution and the alkaline solution of ethyl alcohol.

5. *Reagents used.* (a) 1*N* HCl solution; (b) Hydrosulphite solution: 0.5 g of sodium hydrosulphite are dissolved in 100 ml of a 0.3% aqueous solution of NaOH; (c) H_2O_2 solution: one volume of perhydrol (100% by volume) is diluted in one volume of H_2O; (d) Diluted solution of potassium ferrocyanide.

Procedure followed. Of the different chromatographic methods in use we chose, for its simplicity and for its high rate of development and examination, the one on circular paper described by RUTTER[4].

Two parallel cuts, about 2 mm apart, are made from the same edge up to the centre of an 11-cm circular filter paper, and the wick so formed is bent at the joint perpendicular to the plane of the paper and cut down to approximately 1.5 cm in length.

0.005 ml of the solution (or of the extract) is then placed on the joint and air-dried.

The wick is then immersed in the developing solvent contained in a small capsule inside a Petri dish, the sides of which support the filter paper in horizontal plane. A glass plate is then placed on the filter paper to retard evaporation, and the time is marked.

Six chromatograms are simultaneously made for each type of ink. Development time 1 hour.

Chromatograms and their examination. Filter paper No. 1101. Developing solvent *n*-butanol-acetic acid.

(Abreviations: U.V. = ultraviolet light; fluor. = fluorescence; m. = moist paper; a.d. = air-dried paper; sol. = solution).

The following zones, that are common to all the chromatograms, are examined: Initial zone or spot, internal circular zone, external zone.

Inks	*Reagents*	*Initial zone or spot*	*Internal circular zone*	*External zone*
Carter's blue-black	after development	slightly blue	invisible	yellowish
	under U.V.	no fluor.	blue-violet (a)	fluor.
	KOH sol.: m.	violet shadow	invisible	white
	,, ,, : a.d.	initial blue colour	,,	yellowish
	U.V.	very little fluor.	violet shadow	fluor.
	hydrosulphite: m.	partial decolour.	invisible	white
	,, : a.d.	slightly blue	,,	yellowish
	U.V.	little fluor.	violet shadow	fluor.
	H_2O_2 sol.: m.	invariable	invisible	white
	,, ,, : a.d.	,,	,,	yellowish
	U.V.	very little fluor.	,,	fluor.
	ferrocyanide sol.: a.d.	undistinguishable	blue-green	yellowish
	U.V.	very little fluor.	hardly visible	fluor.
Carter's blue-rex	after development	slightly blue	slightly blue	green-yellowish
	U.V.	intense fluor.	two zones: internal blue external white	little fluor.
	KOH sol.: m.	slightly reddish	decolouration	white
	,, ,, : a.d.	decolour., almost	,,	green-yellowish
	U.V.	total fluor.	visible	fluor.
	hydrosulphite: m.	decolouration	decolouration	white
	,, : a.d.	,,	,,	green-yellowish
	U.V.	fluor. (b)	little fluor.	fluor.
	H_2O_2 sol.: m.	invariable	invariable	white
	,, ,, : a.d.	partial decolour.	partial decolour.	green-yellowish
	U.V.	intense fluor.	visible	fluor.
	ferrocyanide sol.: a.d.	undistinguishable	blue-green	yellowish
	U.V.	little fluor.	visible	intense fluor.
Pelikan	after development	blue	thick, slightly blue	yellowish
	U.V.	intense fluor.	little fluor.	fluor.
	KOH sol.: m.	slightly reddish	decolouration	white
	,, ,, ,,: a.d.	slightly blue-green	,,	yellowish
	U.V.	intense fluor.	visible	fluor.
	hydrosulphite: m.	decolour., almost	total decolour.	white
	,, : a.d.	total slightly reddish	,, ,,	yellowish
	U.V.	intense fluor.	visible	fluor.
	H_2O_2 sol.: m.	invariable	invariable	white
	,, ,, : a.d.	partial decolour.	partial decolour.	yellowish
	U.V.	fluor.	hardly visible	fluor.
	ferrocyanide sol.: a.d.	undistinguishable	thick, blue-green	yellowish
	U.V.	little fluor.	hardly visible	intense fluor.

(a) Distinguishable better under diffuse light.
(b) Particularly toward the circumference.

Inks	*Reagents*	*Initial zone or spot*	*Internal circular zone*	*External zone*
Parker Quink washable blue	after development	blue	blue	yellowish
	U.V.	intense fluor.	little fluor.	fluor.
			externally	
	KOH sol.: m.	reddish hardly	reddish	white
	,, ,, : a.d.	visible intense	decolouration	yellowish
	U.V.	irregular fluor.	fluor. externally	fluor.
	hydrosulphite: m.	total decolour.	total decolour.	white
	,, : a.d.	,, ,,	,, ,,	yellowish
	U.V.	intense fluor.	little fluor.	little fluor.
	H_2O_2 sol.: m.	invariable	invariable	white
	,, ,, : a.d.	partial decolour.	partial decolour.	yellowish
	U.V.	little fluor.	fluor. externally	fluor.
	ferrocyanide sol.: a.d.	undistinguishable	green, little fluor.	yellowish
	U.V.	little fluor.	externally	intense fluor.
Parker Quink, permanent blue	after development	blue	blue	yellowish
	U.V.	fluor.	fluor. externally	fluor.
	KOH sol.: m.	blue	slightly reddish	white
	,, ,, : a.d.	,,	hardly visible	yellowish
	U.V.	fluor.	fluor. externally	fluor.
	hydrosulphite: m.	slightly blue	total decolour.	white
	,, : a.d.	,, ,,	,, ,,	yellowish
	U.V.	fluor.	fluor. externally	fluor.
	H_2O_2 sol.: m.	blue	blue	white
	,, ,, : a.d.	slightly blue	slightly blue	yellowish
	U.V.	little fluor.	little fluor.	fluor.
	ferrocyanide sol.: a.d.	undistinguishable	blue-green	yellowish
	U.V.	little fluor.	little fluor.	intense fluor.
			externally	
Elvita	after development	blue	thick, slightly blue	yellowish
	U.V.	intense fluor.	very little fluor.	fluor.
	KOH sol.: m.	bright-red	decolouration	white
	,, ,, : a.d.	slightly blue	,,	yellowish
	U.V.	intense fluor.	blue-violet shadow	fluor.
	hydrosulphite: m.	hardly visible	decolouration	white
	,, : a.d.	slightly reddish	,,	yellowish
	U.V.	intense fluor.	little fluor.	intense fluor.
	H_2O_2 sol.: m.	invariable	invariable	white
	,, ,, : a.d.	partial decolour.	partial decolour.	yellowish
	U.V.	intense fluor.	little fluor.	intense fluor.
	ferrocyanide sol.: a.d.	undistinguishable	thick, blue-green	yellowish
	U.V.	intense fluor.	hardly visible	intense fluor.

Inks	*Reagents*	*Initial zone or spot*	*Internal circular zone*	*External zone*
Menounos	after development	blue	blue, little fluor.	yellowish
	U.V.	very intense fluor. red-brown	externally	little fluor.
	KOH sol.: m.	greenish traces	reddish hardly	white
	,, ,, : a.d.	intense fluor.	visible	yellowish
	U.V.		decolouration fluor. externally	little fluor.
	hydrosulphite: m.	decolouration	decolouration	white
	,, : a.d.	,,	,,	yellowish
	U.V.	fluor. particul. externally	fluor. externally	fluor.
	H_2O_2 sol.: m.	invariable	invariable	white
	,, ,, : a.d.	partial decolour.	partial decolour.	yellowish
	U.V.	fluor.	little fluor. externally	fluor.
	ferrocyanide sol.: a.d.	undistinguishable	blue-green	yellowish
	U.V.	fluor.	visible	intense fluor.
Menounos, common	after development	slightly blue	slightly blue	yellowish
	U.V.	little fluor. externally	visible	fluor.
	KOH sol.: m.	slightly reddish	total decolour.	white
	,, ,, : a.d.	hardly visible	,, ,,	yellowish
	U.V.	little fluor. externally	hardly visible	fluor.
	hydrosulphite: m.	almost total decolour	decolour.	white
	,, : a.d.	hardly visible	,,	yellowish
	U.V.	fluor. externally	hardly visible	fluor.
	H_2O_2 sol.: m.	invariable slightly	invisible	white
	,, ,, : a.d.	blue little	,,	yellowish
	U.V.	fluor. externally	,,	fluor.
	ferrocyanide sol.: a.d.	undistinguishable	green	yellowish
	U.V.	no fluor.	visible under diffuse light	fluor.

DISCUSSION

Besides the afore-mentioned reagent solutions, the following were also used, unsuccessfully: ammoniacal solution of $AgNO_3$, aqueous solution of bromine, $FeCl_3$ solution, and diluted acid solution of $KMnO_4$. Ammonia vapours decolour the initial spot reversibly.

(2) The R_F values have not been calculated (a) because, as mentioned, we did not try in this essay to make a systematic study of the various inks, and (b) because, dealing with products of not standard properties, the values could possibly vary.

(3) In consideration of the difficulty of working always in same conditions (same length and width of the wick, same temperature, *etc.*) and in order to avoid the formation of chromatograms of different dimensions, one could neglect the time factor and take care rather of the diameter of the chromatogram which must always be the same. We note in this connection the communication of SAIFER AND ORESKES[5] who reached the conclusion that of the various factors, the length of the wick and the temperature, influence the uniformity (R_F value) of the chromatograms.

SUMMARY

Circular paper chromatography according to RUTTER's method, which gives excellent results for the comparative study of very small quantities of a given substance, has been of considerable help for the characterization of inks for criminological purposes. The quantities of ink examined correspond to 0.0001 ml. Chromatograms were studied by means of ultraviolet light using various reagent solutions: sodium hydrosulphite, potassium hydroxide, hydrogen peroxide, and potassium ferrocyanide.

RÉSUMÉ

La chromatographie circulaire sur papier, d'après la méthode de RUTTER, donnant d'excellents résultats lors d'études comparatives de très faibles quantités d'une substance donnée, s'est montrée très utile pour la caractérisation des encres. La quantité d'encre nécessaire est de 0.0001 ml. Les chromatogrammes ont été examinés en lumière ultraviolette, au moyen de diverses solutions de réactifs: hydrosulfite de sodium, hydroxyde de potassium, peroxyde d'hydrogène et ferrocyanure de potassium.

ZUSAMMENFASSUNG

Die Kreis-Papier-Chromatographie, nach der Methode von RUTTER, welche bei vergleichenden Untersuchungen von sehr kleinen Quantitäten einer gegeben Substanz ausgezeichnete Resultate gibt, zeigt sich als sehr nützlich zur Charakterisierung von Tinten. Die notwendige Quantität Tinte ist 0.0001 ml. Die Chromatogramme wurden geprüft in ultraviolettem Licht, mit Hilfe verschiedener Lösungen von Reaktiven: Natriumhydrosulfit, Kalilauge, Wasserstoffsuperoxyd und Kaliumferrocyanid.

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THE DETERMINATION OF SMALL QUANTITIES OF METAL IONS USING ANTHRANILIC ACID

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INTRODUCTION

The use of organic compounds as precipitating ag nts in inorganic gravimetric analysis is well established. 8-hydroxyquinoline is the best known example and the insoluble complexes it forms with metals have, in addition, been dissolved and the determination completed either titrimetrically or by absorptiometry. The usual titrimetric procedure is that of bromination, but a method using cerate has been evolved by GERBER, CLAASEN AND BORUFF[1] for small amounts of magnesium in plant materials. These authors have also described an absorptiometric procedure using the ferric complex. Other absorptiometric methods are known, such as that of DAVIDSON[2] who used the ultra-violet absorption spectrum of 8-hydroxyquinoline itself.

Since anthranilic acid is a useful gravimetric reagent the present authors thought it desirable to determine how far such methods can be applied to it. That involving bromination has already been investigated by CIMERMAN AND SELZER[3], but cerate oxidation could offer advantages for small amounts of metal ions if the equivalence ratio were as high as it is in the case of 8-hydroxyquinoline. Hence it was decided to investigate cerate oxidation and spectrophotometric procedures.

CERATE TITRATIONS

GERBER, CLAASEN AND BORUFF, using 8-hydroxyquinoline, dissolved the precipitated metal complex in acid, reacted it with excess cerate at 95°-100° and determined the excess by back-titration with oxalate. Consistent results were given with perchloratocerate but not with perchloratosulphate.

In our work perchloratocerate was always used, since it has the higher oxidation potential.

Reagents

0.01 N perchloratocerate in 2 N perchloric acid.

Setapoline C, 0.1% in water. The indicator was heated on the water bath each day before use.

0.05 M 5-nitroferroin.

0.01 N sodium oxalate in 2 N perchloric acid.

Anthranilic acid. Standard solution, just sufficient sodium hydroxide being used to effect complete solution.

Determinations using anthranilic acid

Aliquots of anthranilic acid solution equivalent to 700 μg of the acid were added to 25 ml cerate solution. The solutions were heated in an oven at 95° for varying lengths of time, then immediately cooled and titrated. Either Setapoline C or 5-nitroferroin could be used as indicator if added near the end of the titration; the amount added was not critical. Of the two we preferred the latter.

The reduction in acid strength caused by the addition of anthranilate as solution was not significant since the redox potential of the system does not vary over the range 1-2*N* perchloric acid.

The blank to be used was not obvious; it was neither the value given by a straight titration of 25 ml cerate against oxalate, nor that after heating for a given time in the oven, but something between them, if they differed. The two figures were not identical, the titre falling by 0.2 ml after heating in the oven for 60 minutes. In these experiments the mean was taken, the error involved being less than that of the determination.

Results using 700 μg are given in Table I.

TABLE I

Heating time (min)	*Equivalents of cerate used per mole of anthranilic acid*						*Average equivalence ratio*	*Standard deviation*
15	16.6,	16.4,	15.9,	15.9,	16.1,	16.1,	16.2 ± 0.4	0.21
	16.2,	16.4,	16.0,	16.2,	16.3,	16.0.		
30	19.3,	19.3,	20.0,	19.9,	18.9,	19.2,		
	19.6,	19.2,	19.4,	19.5,	18.6,	18.5,	19.3 ± 0.8	0.39
	19.4,	19.4,	19.5,	19.4.				
60	20.8,	20.8,	20.8,	21.0,	20.6,	20.7,		
	21.0,	20.7,	21.0,	21.1,	20.9,	21.0,	20.9 ± 0.3	0.16
	21.0,	20.6,	20.8,	20.7.				
120	21.8,	21.7,	22.1,	22.2,	21.9,	22.1,		
	22.1,	22.1,	22.4,	22.0,	22.1.		22.0 ± 0.4	0.19
240	22.6,	22.7,	22.2,	22.5,	22.4,			
	22.3,	22.5.					22.5 ± 0.3	0.16

The rate of change of the equivalence ratio was found graphically to be about 0.085 a minute after 30 minutes heating and 0.025 a minute after 60 minutes. Hence 60 minutes was adopted as a suitable standard heating time.

It was found that the reaction also proceeded in the cold, although more slowly. This is illustrated briefly in Table II.

TABLE II

Reaction time (min)	*Equivalence ratio*
15	13.0
30	13.7
60	14.6
120	15.5

For this reason it was inadvisable to allow the cerate-anthranilate solution to stand for long periods before heating or titrating.

It was noticed that, especially in the cold, a green colour often formed as soon as anthranilate was added to the cerate solution. It quickly disappeared and was replaced by a deepening of the cerate colour; this gradually faded but it would have obscured the end-point had any attempt been made to perform the titration after simply standing at room temperature for a short time. The colours were presumably due to the formation of cerium-anthranilic acid complexes.

Variation in the quantity of anthranilic acid used showed that as the relative amount decreased the oxidation became slightly more rapid and the equivalence factor for a given time increased. As the amount taken varied from 1000 μg to 150 μg the equivalence factor varied from 20.8 to 21.8. The use of an average factor would increase the error at the extremes to about 5%, whereas using a calibration curve would reduce it to about 1%.

METAL ANTHRANILATES

Having established the reproducibility of the oxidation, its application to the metal anthranilates was investigated.

Known amounts of copper or zinc ions were precipitated as anthranilate in a 25 ml centrifuge tube according to the method of Cimerman and Wenger. In each case the precipitate was centrifuged in an International No. 1 Centrifuge for 10 minutes at 2000 r.p.m.; to ensure a clean separation one drop of 1% Cetavolon solution (I.C.I. Ltd.) was added to the tube initially. After centrifuging, the supernatant liquid was discarded and the precipitate washed four times with about 1 ml of ethanol to remove excess anthranilic acid. After washing it was dissolved in a few ml of 2*N* perchloric acid and the anthranilic acid determined using perchloratocerate.

Using the known composition of the anthranilate the equivalence factor was calculated for zinc and copper. Within the experimental error given previously it was, in both cases, twice that for anthranilic acid itself, over a similar range of concentrations. Hence the method may be assumed to be valid for the determination of metals which give insoluble anthranilates, and in the approximate range 1-5 micromoles of metal. There seems no reason why smaller quantities should not be determined in this way but the blank determination would increase in importance and it would be desirable to reduce the scale of the titrations. We did not do this since the absorptiometric method seemed preferable.

The possibilities of determinations when more than one precipitable ion was present were also investigated; they are discussed in the section dealing with absorptiometric procedures.

ABSORPTIOMETRIC PROCEDURES

Reagents

Dilute (3*N*) hydrochloric acid.
2% sodium nitrite solution.
4% ammonium sulphamate.
0.1% *N*-(1-naphthyl) ethylenediamine hydrochloride in water.

EXPERIMENTAL

Determinations using anthranilic acid

Since anthranilic acid has an amino group it is possible to diazotise and couple it. It was found that coupling with N-(1-naphthyl) ethylenediamine gives a brilliant purple colour which, with the quantities used, develops its maximum intensity in less than twenty minutes. The absorption curve of the solution is given in Fig. 1. The maximum absorption is at 550 mμ and further work was carried out using a Spekker Absorptiometer, 1 cm cells, and an Ilford 605 filter (max = 550 mμ).

To a measured quantity of cooled anthranilate solution was added excess (about three drops total amount) of freshly prepared 2% sodium nitrite solution, and the excess destroyed by adding 2 ml of 4% ammonium sulphamate solution. The colour was then developed by adding 0.5 ml of the reagent and its absorption measured after standing for not less than twenty minutes, diluting if necessary.

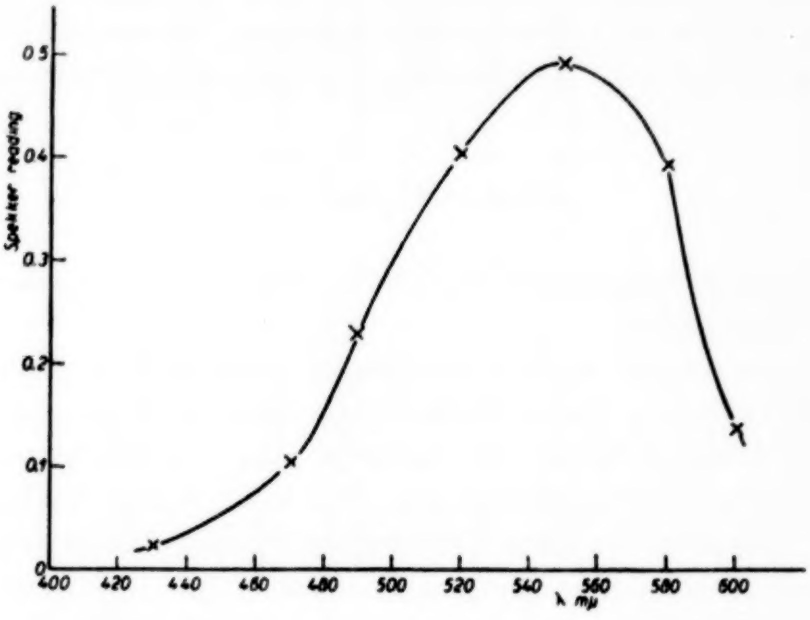

Fig. 1. Absorption curve of the solution of anthranilic acid, after diazotation, with N-(1-naphthyl) ethylenediamine.

TABLE III

Zinc taken (μg)	*Zinc found (μg)*			
31.5	31.0,	30.0,	30.3,	32.0,
	31.5,	30.9		
18.9	18.6,	19.1,	18.4,	18.9,
	18.4			
	18.3,	19.4,	19.4,	18.5
	18.4			
12.6	12.4,	12.5,	13.3,	12.4
	12.4,	13.4,	12.6	
6.3	6.3,	6.3		

It was found that

(1) Up to a thousand-fold excess of sodium nitrite could be used without any variation of the final reading, provided that care was taken to destroy the excess.

(2) The colour was stable for at least fifteen hours.

(3) Beer's Law was obeyed over the concentration range convenient for the instrument and cell size — 0.64-3.84 μg anthranilic acid per ml.

(4) The lowest amount which could reasonably be determined in a 1 cm cell was of the order of 0.5 μg per ml.

Having established the validity of the method for anthranilic acid, metal anthranilates were formed by precipitation, centrifuged and washed as described previously, then dissolved in about 1 ml of dilute hydrochloric acid. The determinations were completed absorptiometrically. Consistent results were obtained as illustrated for zinc in Table III.

References p. 141

Among the commonly used metals we found that the following gave precipitates with anthranilic acid when present to the extent of a few milligrams per ml — copper, zinc, cadmium, manganese, nickel, cobalt, lead, mercury, silver and uranyl. Aluminium, magnesium, chromium, ferrous and ferric iron, molybdenum, tungsten and vanadium gave no precipitates, although they might have done so from more concentrated solutions.

For the determination of copper in the presence of other precipitable metals use was made of the fact that the copper compound is by far the least soluble in acetate buffers. The solubility of the complexes in such buffers increases with increasing acetate concentration as has been shown by Holmes and Reed[4].

Determinations were carried out as previously except that before precipitation there was added 1 ml of a sodium acetate solution of known concentration, adjusted to a pH of between 6 and 7. Typical results for copper and zinc using different strengths of sodium acetate are given in Table IV.

TABLE IV

Metal	*Grams of crystalline sodium acetate per litre*	*µg metal taken*	*µg metal recovered*
Copper	100	25.0	24.6
		50.0	49.5
	200	50.0	49.6
Zinc	100	40.0	29.2
		50.0	34.0
		60.0	46.0
		80.0	61.7
	200	30.0	nil.
		40.0	nil.
		60.0	4.8
		80.0	14.8

The other anthranilates used were much more soluble in acetate solutions, and using a 200 gram per litre buffer no recovery was obtained from 100 µg of cobalt, nickel, cadmium, manganese, lead or mercury.

Thus copper could be determined in the presence of other metals if the amount of these, and especially of zinc, was not excessive. A five-fold excess of zinc and at least ten-fold excess of the others might be permissible. The limits were not sought more precisely. A few such determinations were satisfactorily performed as illustrated in Table V.

TABLE V

Copper taken (µg)	*Zinc taken (µg)*	*Metal found (µg)*
18.9	18.9	18.4, 18.3, 18.7 18.7, 19.3 19.5
37.8	37.8	37.8, 37.4 37.4, 38.3

References p. 141

It should be noted that the lowest pH of complete precipitation of metal anthranilates is not normally greater than five, and in many cases it is much less; nevertheless precipitation was always carried out in a solution of pH between 6 and 7.

In a mixture containing copper and a second precipitable metal it would seem that both could be determined. This might be done either by performing two precipitations, one with sodium acetate present and the other in its absence, or by precipitating the mixed solution and extracting the precipitate with sodium acetate. Neither of these possibilities was investigated since the authors were concerned with the general principles.

FLUORIMETRY

Anthranilic acid solutions in water and ethanol were each compared with a quinine standard using a Spekker Fluorimeter. The fluorescence in ethanol was several times as great as that in water. However, anthranilic acid does not fluoresce in acid solutions, in which measurements are most conveniently made, and the method was not studied further, absorptiometry having previously proved satisfactory.

SUMMARY

Metal ions which form insoluble anthranilates may, if present singly, be determined by dissolving the anthranilate in acid and titrating the liberated anthranilic acid with perchloratocerate. Or preferably the anthranilic acid may be determined absorptiometrically with N-(1-naphthyl) ethylenediamine hydrochloride after diazotisation. Under the conditions described quantities of the order of 1-5 micromoles of metal are conveniently determined by the volumetric method and one fifth of such amounts by absorptiometry. With the latter the use of larger Spekker cells would increase the sensitivity of the method.

By making use of the insolubility of its complex in acetate buffers copper may be determined in the presence of other metals if these are not in excessive amounts. Various other determinations are also possible.

Attempts to use the fluorescence of the liberated anthranilic acid have indicated the method to be less satisfactory than absorptiometry.

RÉSUMÉ

Les cations formant des anthranilates insolubles peuvent être dosés individuellement par dissolution de leur anthranilate dans un acide et titration de l'acide anthranilique libéré par un perchloratocérate. L'acide anthranilique peut être dosé encore, de préférence, par absorptiométrie au moyen de chlorhydrate de N-(1-naphtyl) éthylène-diamine, après diazotation. Dans les conditions décrites, des quantités de l'ordre de 1-5 micromoles du métal peuvent être dosées par la méthode volumétrique et le cinquième de cette quantité par la méthode absorptiométrique. Avec cette dernière, la sensibilité de la méthode pourrait être augmentée en utilisant des cuves Spekker plus grandes. Grâce à l'insolubilité de son complexe en tampons acétiques, le cuivre peut être dosé en présence d'autres métaux, à condition que ceux-ci ne soient pas en trop forte teneur. Différents autres dosages sont également possibles. Des essais basés sur la mesure de la fluorescence de l'acide anthranilique ont démontré que cette méthode est moins satisfaisante que celle par absorptiométrie.

ZUSAMMENFASSUNG

Die Metallionen, welche unlösliche Anthranilate bilden, können einzeln durch Auflösung des Anthranilates in einer Säure und durch Titration der freien Anthranilinsäure mit Perchloratocerat bestimmt werden. Die Anthranilinsäure aber, kann vorzugsweise auch noch durch Absorptiometrie mit Hilfen von N-(1-Naphtyl) Äthylendiaminchlorhydrat, nach Diazotation bestimmt werden. In den beschriebenen Bestimmungen können Quantitäten von Metall in der Grössenordnung von 1-5 Mikromol bestimmt werden mit der volumetrischen Methode, und ein fünftel dieser Quantität mit der absorptiometrischen Methode. Für diese letzte könnte die Empfindlichkeit erhöht werden, indem man grössere Spekker-Zellen verwenden würde. Dank der Unlöslichkeit seines Komplexes

im Acetatpuffer, kann das Kupfer in Gegenwart anderer Metalle bestimmt werden, unter der Bedingung, dass diese in nicht zu grossen Mengen vorhanden sind. Verschiedene andere Bestimmungen sind ebenfalls möglich. Die Versuche, die auf der Messung der Fluoreszenz der Anthranilinsäure basieren, haben gezeigt, dass diese Methode weniger befriedigend ist, als die Absorptiometrie.

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ALIZARIN-S, A REAGENT FOR THORIUM.
A GRAVIMETRIC, COLORIMETRIC, AND SPECTROPHOTOMETRIC STUDY

by

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BECK[1] suggested the separation of scandium and thorium from rare earths by precipitation with 2.5 % alizarin-S solution and subsequent treatment with 30 % acetic acid. The experimental details are not available and preliminary experiments indicated that the thorium alizarin-S complex dissolves appreciably even in very dilute acetic acid. A further investigation was undertaken adopting the following procedure.

Precipitation of thorium with alizarin-S

10 ml of pure thorium nitrate containing 0.0687 g of ThO_2 were pipetted into a 400 ml beaker to which were added 10 ml of 50% ammonium nitrate and the desired quantity of 2*N* acetic acid. The mixture was diluted to about 190 ml and heated to boiling. 10 ml of 2.5 % alizarin-S were added in a thin stream with continuous stirring. The slimy precipitate was allowed to settle, filtered through Whatman No. 42 and washed with 5 % ammonium nitrate acidified with a few drops of 2*N* acetic acid. The precipitate was ignited at 900 to 1000 ° C and weighed as ThO_2.

TABLE I

EFFECT OF ACETIC ACID ON THE PRECIPITATION OF THORIUM
ThO_2 taken: 0.0687 g

Volume of 2N acetic acid added ml	*Wt of ThO_2 found* g*	*Difference mg*
10	0.0686	—0.1
20	0.0687	—
30	0.0677	—1.0
50	0.0575	—11.2
70	0.0484	—20.3

* Mean of three determinations.

The maximum amount of free acetic acid that the thorium complex can tolerate is thus 0.2*N*.

When dilute HCl was substituted for acetic acid, the amount of free acid that could be present for complete precipitation was even less. Experiments with the cerite earths showed that there was appreciable precipitation of these latter in the presence of 30 ml of acetic acid, *i.e.*, in solutions 0.3*N* in acetic acid.

Thus the reagent does not appear to be suitable for the gravimetric separation of thorium from the cerite earths.

Colorimetric estimation of thorium with alizarin-S

MURTHY AND RAO[2] developed a colorimetric procedure for the estimation of thorium in the presence of cerite earths based on an earlier observation of GERMUTH AND MITCHELL[3]. In this method the colour of the test sample was compared with that of a known standard and Beer's law was tacitly assumed for narrow concentration ranges. The amount of thorium that could thus be estimated was confined to a narrow range 0.2 to 0.5 mg in 20 ml. A detailed investigation of this colour reaction seemed warranted.

Alizarin-S gives a red colour with thorium which is not however specific. The cerite earths behave similarly, but a condition may be established when thorium alone reacts and the cerite earths do not interfere in 10-fold excess[2]. For a complete understanding of this reaction, data on the optical characteristics of the reagent as well as of the thorium complex, particularly their dependance on pH, are essential.

Absorption spectra. Absorptions were studied with a D.U. model Beckman quartz spectrophotometer. The liquids were taken in matched corex glass cuvettes of 10 mm optical path. Absorption measurements were made at suitable wave-length intervals. The spectral band was always limited to a workable minimum lying between 0.7 mμ at the more refrangible end and 2.0 mμ at the other.

Measurements of pH were made with a Cambridge bench type pH meter employing a glass electrode against a saturated calomel element. About 15 minutes were allowed for the glass electrode to attain equilibrium.

Fig. 1. shows the transmission characteristics of the reagent alizarin-S and of the thorium complex.

Reagent: pH 2.0, concentration: 19.5 mg per litre.

Complex: pH 2.0, concentration: 19.5 mg of reagent + 14.8 mg of Th per litre.

An examination of the two curves shows that in complex formation the absorption is displaced laterally to longer wave-lengths. The wave-length 520 mμ appears to be best suited for measurements.

Validity of Beer's law: (a) *Reagent*: Below pH 3.3 and between 600 and 500 mμ alizarin-S has no measurable absorption in concentrations up to 780 mg per litre which is much above the concentration employed in colorimetric work. Further its absorption at all wave-lengths obeys Beer's law in amounts up to 390 mg per litre.

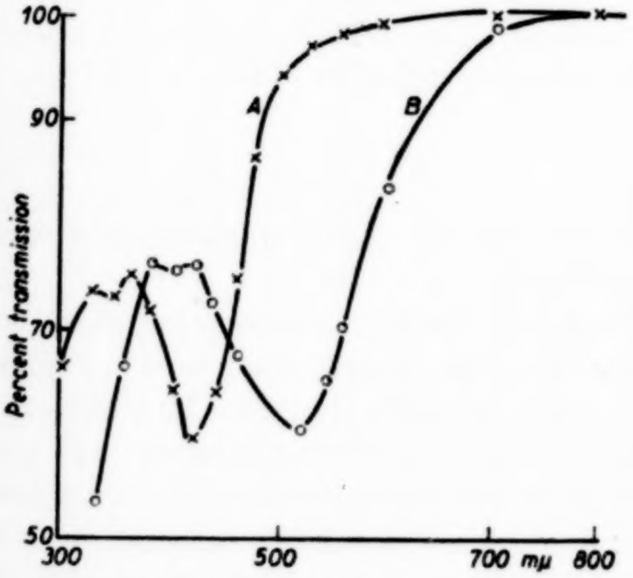


Fig. 1. Transmission of (A) alizarin-S, (B) Th-alizarin-S.

(b) *Complex*: The Beer's law plot of the complex, or what may be termed a working curve, was obtained by mixing different amounts of thorium nitrate with 3.9 mg of alizarin-S in 5 ml of 0.1 *N* HCl making up the volume to 50 ml and measuring its density at 520 mμ. The colour is developed immediately and is stable for 48 hours, except in very concentrated solutions when precipitation occurs.

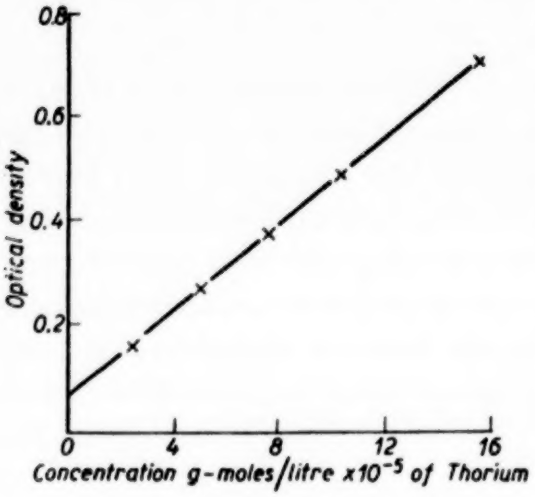


Fig. 2. Beer's Law plot.

The results are shown in Fig. 2. Quantities from 0.01-6.3 mg of thorium in 50 ml may thus be conveniently estimated.

Interference from cerite earths. Two test solutions containing 0.687 mg of ThO_2; and 22.35 mg and 8.94 mg respectively of R_2O_3 (cerite earths from monazite) gave transmissions 53.6 % and 55.4 % against 55.6 % of the pure thorium solution densities 0.2708, 0.2565 and 0.2549 respectively. Interpolation in Fig. 2 gives ThO_2 = 0.730 mg, 0.688 mg and 0.687 respectively. While large amounts of cerite earths give rise to higher values of thorium, amounts in quantities likely to occur in monazite (about 13 to 14 fold excess) have practically no effect on the estimation.

Estimation of thorium in monazite. A sample of monazite 4.000 g was decomposed with sulphuric acid and freed from Zr^{+4}, PO_4^{-3} *etc.* by double precipitation with oxalic acid in acid medium. The oxalates were digested with fuming nitric acid and evaporated to dryness on a water bath, after reduction of Ce^{+4} with H_2O_2. The residue was extracted with water and made up to 50 ml. 10 ml of this solution were further diluted to 1000 ml.

5.0 ml of the diluted solution were complexed with 3.9 mg of the reagent, diluted to 50 ml at pH 2.8 and its absorption at 520 mμ was measured as 75.0 % or density 0.1245 on the average in four different aliquots. This corresponds to 0.0636 mg per ml or 0.3180 g of ThO_2 in the total amount of monazite, *i.e.*, 7.95 % of ThO_2. A gravimetric estimation by double precipitation with sebacic acid gave ThO_2 = 7.87 %.

Structure of the thorium-alizarin-S complex

The composition of the complex was studied by several optical methods and was also confirmed gravimetrically by semi-micro methods.

(a) JOB's *method of continuous variations*[4]. Alizarin-S shows an absorption peak at 418-420 mμ, which disappears on complex formation. The transmission in this region rises to a maximum when all the reagent has complexed with thorium. This increase in transmission is also proportional to the amount complexed. Thus the region 418-420 mμ is as much suited for investigations of structure as 520 mμ where the complex shows maximum absorption. Plots of the Y function *i.e.* observed densities corrected by the densities due to components, against concentration of the components are shown in Fig. 3, both at 420 and 520 mμ. The curve at 420 passes through a minimum while that at 520 mμ through a maximum. In both cases the inflection occurs at molar ratios of 1 : 1.1 or 1 : 1 nearly. This concurrence of inflection at two wave-lengths is also an indication that only one complex is formed. The molar ratio[5] and slope ratio[6] methods gave the same result.

(b) A variant of the slope ratio method which has been employed in this laboratory is to plot from two origins at the opposite ends of the X- axis to the same scale. The point of intersection gives the molar ratio of the components. This is shown in Fig. 4.

(c) *Gravimetric determination.* (i) The thorium-alizarin-S complex was precipitated from

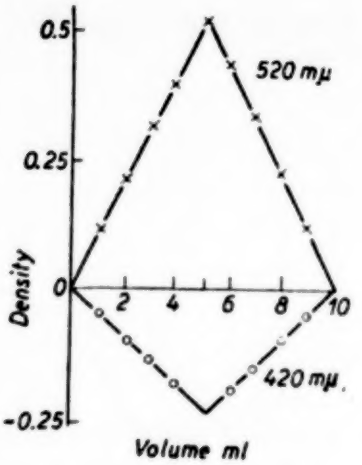


Fig. 3. Job's method.

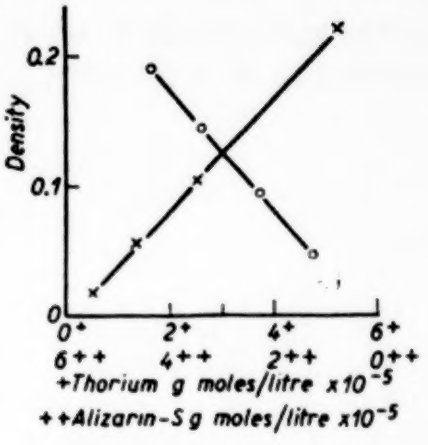


Fig. 4. Modified slope ratio method.

concentrated solutions and after complete washing was dried to constant weight at 110° ± 2° C. Known amounts of the dried complex were ignited to the oxide and weighed. From these weights, thorium: alizarin-S ratio was computed as shown in Table II.

TABLE II

GRAVIMETRIC COMPOSITION OF THORIUM-ALIZARIN-S

S. No.	*Wt of complex taken (g)*	*Wt of ThO_2 found (g)*	*Molar ratio of Th to alizarin-S*
1	0.2422	0.1105	1 : 1.023
2	0.3288	0.1532	1 : 1.001
3	0.6543	0.3044	1 : 1.003

(ii) *Gravimetric-optical method.* 1.99 mg of dried complex was boiled with water and after the entire complex has been dispersed into solution, 5 ml of 0.1*N* HCl were added and diluted to 50 ml. The optical density of this suspension was measured at 520 mμ, which gave the value 0.2882. This gives on interpolation in Fig. 2 a content of 0.9275 mg of ThO_2 in 50 ml. The corresponding weight of the complex on a 1 : 1 ratio of thorium to the dye ligand is 1.986 mg, which compares very favourably with the amount taken, 1.99 mg.

Fig. 2 was drawn from data obtained in the presence of excess of the reagent. The reagent no doubt has no measurable absorption at 520 mμ. However in the presence of excess reagent the equilibrium, Th + Al-S ⇄ Th — Al-S, is shifted towards the right, resulting in increased formation of the complex. The effect of this would be to give lower values for thorium. The close agreement in the thorium values suggests that the dissociation of the complex into the components is extremely small. Further evidence in its favour is produced in the following section.

The stability of the complex

With the composition of the complex established, the equilibrium coefficient of the dissociation

$$\mathrm{Th} - \mathrm{Al\text{-}S} \rightleftarrows \mathrm{Th} + \mathrm{Al\text{-}S} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

may be computed as follows.

If c is the concentration of the complex and α its dissociation, then the equilibrium coefficient K is given by

$$K = \frac{(\alpha\ c)^2}{c\ (1 - \alpha)} = \frac{\alpha^2 c}{(1 - \alpha)} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

$$\text{now } \alpha = \frac{D_m - D_s}{D_m} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

Where D_m is the maximum or limiting density of the complex corresponding to a definite amount of thorium with excess alizarin-S and D_S is the density when the same amount of the metal ion reacts with a stoichiometric equivalent of the dye ligand. It is found that

$$D_m = 0.210$$

$$\text{and } D_s = 0.206$$

$$\alpha = 0.019 \text{ and}$$

$$K = 1.914 \cdot 10^{-8}$$

The stability of the complex is known to be very much dependent on pH. In Figs. 5a and 5b are shown the absorptions of the reagent and the complex respectively under different pH conditions. The optical density at 520 mμ gives directly D_s. D_m is the limiting density (*i.e.* at pH 4). The equilibrium coefficient K of the complex at various pH values is calculated and shown in Table III.

TABLE III

PH AND STABILITY OF THE COMPLEX

pH	*Absorption at 520 mμ*	*Density of complex D_S*	*a*	*Equilibrium coefficient K*
0.69	41.0	0.40	0.576	$1.7 \cdot 10^{-1}$
1.5	18.6	0.73	0.226	$1.47 \cdot 10^{-5}$
1.8	14.0	0.854	0.0945	$2.2 \cdot 10^{-7}$
2.7	from above	—	0.019	$1.914 \cdot 10^{-8}$
4.7	11.5	0.939	0.004	$4.0 \cdot 10^{-9}$

The nature of the complex

The likeness ot the curves of Figs. 5a and 5b is very instructive. Complexation with thorium appears to stabilize the structure of the neutral molecule to the extent that complexation has occurred. Thus thorium complex at pH 0.69 and the reagent at pH 3.97 exhibit similar curves. The acid form of the dye undergoes a transformation of the neutral form and the thorium appears to be about half dissociated as one may compute from the absorption at 520 mμ.

Zirconium[7] behaves similarly with the dye. The absorption of the complex occurs at 520 mμ. Further the complex shows increased stability at low pH ranges compared to thorium.

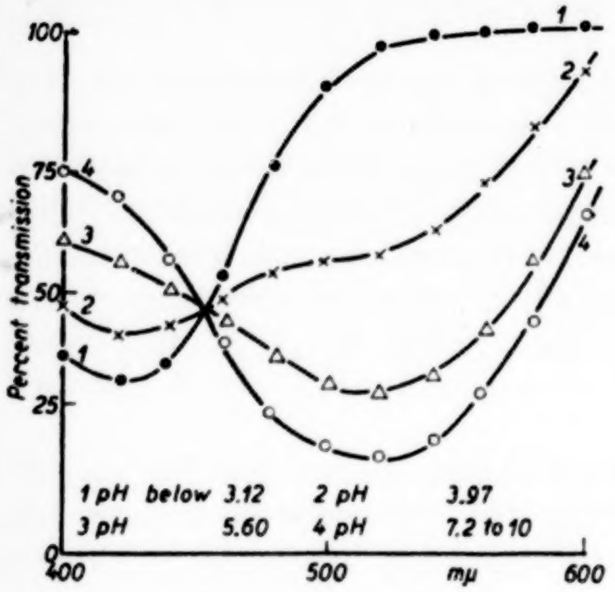


Fig. 5a. Absorption of alizarin-S; variation with pH.

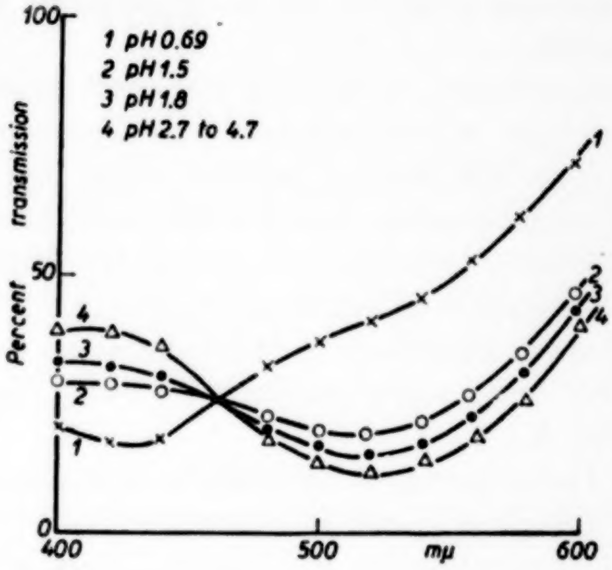


Fig. 5b. Absorption of Th-alizarin-S; variation with pH.

The structure of metal-alizarin complexes

A knowledge of the absorption of the dye in solutions of widely differing pH is of value in this connection. The essential characteristics of this absorption are collected below.

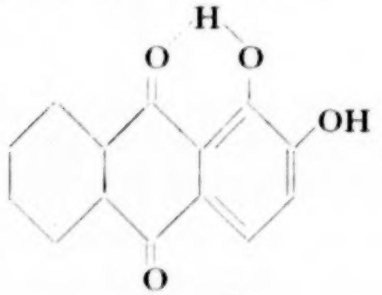
In dil. HCl pH below 2.0	*In dil. ammonia or very dil. sodium hydroxide pH 4-10*	*In dil. alkali (sodium hydroxide, pH 12 and over*
(1) A sharp and intense peak ε(about 3.0) at 266 mμ	No change	No change
(2) A small peak 340 mμ	Intensifies	Intensifies
(3) A peak at 418-20 mμ intensity less than (1) (ε about 0.46)	Shifts to 520 (ε about 0.74)	Shifts and forms a broad band between 600-520 with a peak 550 mμ.

On complexation with thorium or zirconium the intense band (at 266-68) suffers no change in position but its intensity falls to Σ about 1.7 while the second band shifts to 520 with no significant change in intensity. While changes in intensity only speak of the probability of a transition, shifts in absorption result from loading of the vibrating chain or its lengthening. In the latter case a simultaneous change in intensity may also occur.

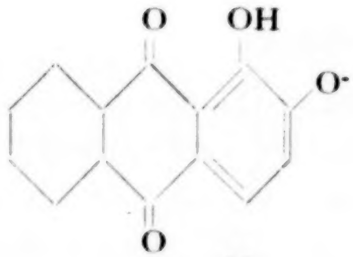
Following KUHN, DORTA-SCHAEPPI[8] *et al.* attempted to explain the first absorption in the visible, of the acid and alkaline forms as well as the lake on the concept of the free electron gas. While the agreement in this respect cannot be deemed satisfactory, the strong absorption in the ultraviolet or the identity of the absorption of the lake with the dye in the pH region 4-10 has not been referred to. The peak at 266 mμ, as has been pointed out, is the strongest and remains unaffected with changes of pH or lake formation. This may be due to absorption by the benzene nucleus to the left of the quinonoid group; benzene has an absorption at 255 mμ; its presence in all subsequent reactions bears this out. The feeble absorption at 340 mμ may arise from the quinonoid group in the 9, 10 positions. This band is affected by acidity and lake formation.

Application of KUHN's procedure to the calculation of the first absorption maxima generally yielded results in good agreement with observations. An important aspect in these calculations, however, is the length of the free electron path. It has been shown by RUEDENBERG AND SCHERR[9] that the free electron path is identical with the bond skeleton except that it exceeds the latter by one bond length at each free end. This additional bond length at the free end should naturally be taken the same as one which preceeds immediately. While the C-C bond length may be taken as 1.39 A, other values have to be employed for such other bonds as C = O, 1.27 A; O-H, 0.96 A and C-O, 1.36 A.

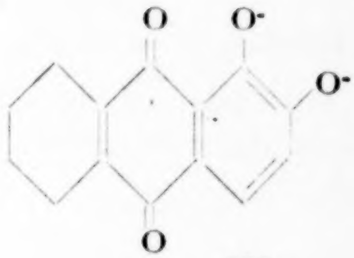
The following structural changes may be envisaged during the reaction. The reagent is a weak acid and is present normally in solution as (II). This is also the structure on lake formation. In acid solution below pH 4.0 the ionization of hydroxyl is suppressed and the acid form develops, structure (I). In strongly alkaline medium, over pH = 12, the two hydroxyls ionize (III).



I

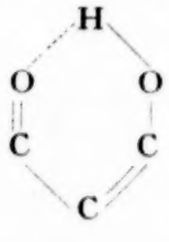


II



III

The vibrating chains responsible for absorption in these three cases are as follows.



I

$HO-C=C-C=C-C=C-\overline{O}$ II

$O=C-C=C-C=C-C=C-\overline{O}$ III

KUHN's equation $\lambda = \frac{8\,mc}{h}\,\frac{L^2}{N+1}$

Where m is the electronic mass; c, the velocity of light; h, Planck's constant; L, the length of the vibrating chain or the free electron path and N is the number of free electrons, applied to the three cases yields the results shown in Table IV.

TABLE IV

CALCULATION OF ABSORPTION MAXIMA

Structure No.	*L in A*	*N*	*Calculated value in mμ*	*Observed value in mμ*
I	8.01*	4	422	420
II	11.39	8	526.9	520
III	13.6	10	554.3	560

* A value of 2.6 A is employed for the length of the (O-H---O)

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The agreement between observed and calculated positions of absorption maxima is as good as may be expected.

SUMMARY

The claim of BECK in the use of alizarin-S for separating cerite earths from thorium could not be substantiated. Detailed conditions for estimating from 0.0095 to 6.3 mg of thorium dioxide in 50 ml of solution by the method of RAO AND MURTHY are described. The absorption characteristics of alizarin-S and its thorium complex have been studied in their dependance on pH. The thorium complex has been shown by adopting different optical methods to correspond to Th-Al-S (a stoichiometric ratio of 1 : 1) which is also confirmed from gravimetric analyses. The dissociation coefficient of the complex at pH 2.7 has been computed to be less than $1 \cdot 10^{-8}$.

RÉSUMÉ

La proposition de BECK pour l'emploi de l'alizarine-S, lors de la séparation des terres cériques et du thorium ne peut se confirmer. Les conditions de dosage du bioxyde de thorium, pour des teneurs allant de 0.0095 à 6.3 mg/50 ml, d'après la méthode de RAO ET MURTHY sont décrites en détail. L'absorption de l'alizarine-S et de son complexe avec le thorium a été étudiée en fonction du pH. Il a été démontré par diverses méthodes optiques que le complexe du thorium correspond à Th-Al-S (rapport stoechiométrique 1 : 1), ce qui est confirmé également par l'analyse gravimétrique. Le coefficient de dissociation du complexe au pH 2.7 a été évalué à moins de $1 \cdot 10^{-8}$.

ZUSAMMENFASSUNG

Die BECKsche Behauptung betreffend der Verwendung des Alizarin-S zur Trennung der Ceriterde von Thor konnte nicht bewiesen werden. Ausführliche Bedingungen zu einer Bestimmung des Thoriumdioxydes von 0.0095 mg bis 6.3 mg in 50 ml Lösung mit dem RAO-MURTHYschen Verfahren werden beschrieben. Es wurden die Absorptions-eigenschaften des Alizarin-S und seines Thorkomplexes, in ihrer Abhängigkeit vom pH untersucht. Durch die Anwendung verschiedener optischen Methoden hat man gezeigt, dass der Thorkomplex Th-Al-S (d.h. einem stöchiometrischen Verhältnis von 1 : 1) entspricht, welches auch durch die Gewichtsanalyse bestätigt wird. Die Dissoziationskonstante der Komplexe bei pH 2.7 hat man auf weniger als $1 \cdot 10^{-8}$ berechnet.

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ERRATUM

Anal. Chim. Acta, Vol. 13 (1955) page 94 in equation line 7 from bottom, for $\dfrac{ic}{2.\mathrm{V}._c}$ read $\dfrac{i_o}{2.V.c.}$.

SPECTROPHOTOMETRIC DETERMINATION OF COPPER WITH HYDROCHLORIC ACID

by

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Previous studies[1,5] have shown that hydrochloric acid is a convenient reagent for the ultraviolet spectrophotometric determination of several elements. In the course of another investigation[3] it became apparent that the absorption of cupric chloride complex ion in the very near infrared (700-1000 mμ) might be used for the spectrophotometric determination of copper with hydrochloric acid. The use of hydrochloric acid as a reagent for copper appears to have been first suggested by HÜTTNER[4]. Much later, GIESECKE[2] pointed out that the color produced is quite stable and that iron need not be be removed. However, very little information is available as to the range and reliability of the method. The study reported here was undertaken to ascertain the conditions under which such a determination might satisfactorily be carried out.

EXPERIMENTAL

Reagents

All solutions except those of actual samples were prepared from reagent grade chemicals and distilled water. Standard solutions of copper and other elements whose spectra or interferences were to be studied were made up by dissolving the required amount of the appropriate salt in distilled water. The solutions taken for spectrophotometric measurements were made by combining aliquots of the standard solutions and diluting to the final volume required to give the desired composition.

Apparatus

The quantitative measurements were made with a Beckman Model B spectrophotometer using matched 1.00 cm Corex cells. All measurements were made using a reference solution containing the same concentrations of reagents as the unknown solution.

Survey of very near infrared spectra

The very near infrared spectra of a series of aqueous solutions of simple inorganic compounds were determined in order to find out which ions show absorption in this region. Of the ions tested, only cupric ion seemed to absorb appreciably. Since the spectra of equal concentrations of cupric chloride, nitrate and sulfate were found to be identical, the absorption appears to be due to the simple, hydrated cupric ion. A list of the compounds which were studied is given in Table I.

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* Taken in part from the thesis submitted by D. G. DAVIS, Jr., in partial fulfillment of the requirements for the B.A. degree with Distinction in Chemistry at Wesleyan University, June, 1954. Present address: Harvard University, Cambridge, Massachusetts, U. S. A.

TABLE I

COMPOUNDS WHOSE VERY NEAR INFRARED SPECTRA WERE DETERMINED

Aluminum iodide
Ammonium molybdate
Ammonium thiocyanate
Antimonous chloride
Arsenic pentoxide
Arsenious acid
Barium chloride
Bismuth chloride
Bromine
Cadmium nitrate
Calcium chloride
*Chromic chloride
*Cobalt nitrate
**Cupric chloride
**Cupric nitrate
**Cupric sulfate
Ferric chloride
Ferric thiocyanate
Ferrous sulfate
Lanthanum nitrate
Lead nitrate
Magnesium nitrate
Manganese nitrate
Mercuric nitrate
*Nickel chloride
*Nickel thiocyanate
*Potassium ferricyanide
*Potassium ferrocyanide
*Potassium permanganate
*Sodium cobaltinitrite
Stannic chloride
Strontium nitrate
Zinc nitrate
*Zinc uranyl nitrate

* indicates slight absorption
** indicates strong absorption

It was also found that in 1:1 hydrochloric acid the very near infrared absorption of cupric ion is greatly enhanced and that of the other ions is not. Of the other ions studied, only ferrous and nickelous ions showed any appreciable absorption in this solvent. The absorption of the chlorocupric ion (probably $CuCl_4^{-2}$) is so much greater that one would expect the determination of copper by means of this absorption to be relatively free of interference.

Effects of chloride and hydronium ion concentration. The effect of the chloride ion upon the copper absorption spectrum was determined by measuring the spectra of a series of solutions kept at constant hydronium ion concentration of 6.0*M* with perchloric acid and containing varying amounts of lithium chloride. Each solution contained 400 p.p.m. of copper. The spectra obtained were similar to those which have been published by WHITE, HEGSTED AND MAYER[7] for copper with varying amounts of hydrochloric acid. The intensity of the very near infrared absorption increases markedly as the chloride ion concentration increases. This is consistent with the assumption that the absorption is due to the chlorocupric ion.

In a similar manner, the chloride ion concentration was maintained constant at 6.0*M* while the hydronium ion concentration was varied from 1.0*M* to 6.0*M*. It was found that these variations in the acidity had little effect upon the absorbancy of the chlorocupric complex ion.

Stability of the color. The color of the complex is yellow-green and is developed immediately. Measurements indicated that the color is stable for at least 24 hours.

Standardized procedure. As a result of the studies of the copper spectrum at different acid and chloride ion concentrations, a standard procedure was evolved for the determination of copper in various samples. As a matter of convenience, 1:1 hydrochloric acid was chosen as the medium. An aliquot of the stock or sample solution containing from 5 to 30 mg of copper was taken, 25 ml of concentrated hydrochloric acid was added, and the solution was diluted to a final volume of 50 ml. The absorbancy at 940 $m\mu$ was then measured at room temperature with the spectrophotometer.

Reproducibility. A statistical study was made of the reproducibility of the absorbancy measurements at 940 $m\mu$ on 25 samples of 400 p.p.m. copper prepared by the above procedure over a period of six days. For the 25 samples, the absorbancy range was 0.524 to 0.566, the average absorbancy was 0.553, and the coefficient of variation was ± 1.9%.

Calibration curve and optimum range. A study of the relationship between the copper concentration and the absorbancy showed that Beer's Law was followed over the range 50 to 1000 p.p.m. of copper. When the data were plotted according to the method of RINGBOM[6], the indicated optimum concentration range was found to be 100 to 600 p.p.m.

Interferences. The effects of a number of cations upon the copper determination were studied, with special attention to those elements which might normally be found in copper-containing alloys or ores. Standard copper solutions were prepared and a large amount of the ion in question was added. From the resulting absorbancy, the ion to copper ratio necessary to cause a 3% error in absorbancy was calculated. The results are shown in Table II.

TABLE II

INTERFERENCES IN THE DETERMINATION OF COPPER WITH 1:1 HYDROCHLORIC ACID AT 940 $m\mu$

Ion	*Ion/Cu Weight Ratio for 3% Error in Absorbancy*	*Direction of Absorbancy Change*
Sn^{+2}	0.03	decrease
Fe^{+2}	0.29	decrease
Ba^{+2}	5	decrease
Al^{+3}	10	increase
Ni^{+2}	10	increase
Pb^{+2}	11	increase
Fe^{+3}	16	increase
Mn^{+2}	16	increase
Cr^{+3}	17	increase
Sn^{+4}	21	decrease
Ca^{+2}	29	increase
Sr^{+2}	36	increase
Cd^{+2}	67	decrease
Hg^{+2}	260	decrease

The most serious interferences were stannous and ferrous ions. Tests showed that these ions were causing the reduction of the cupric ion. The addition of a little ammonium persulfate was found to prevent this interference. In the case of samples which were dissolved in nitric acid, the addition of persulfate was found to be unnecessary because of the oxidizing nature of the acid.

Analysis of samples. In order to test the method, the copper contents of a number of actual samples were determined. It was found that most alloys and ores would dissolve in hot nitric acid. The solution should then be boiled to expel the oxides of nitrogen before the proper amount of concentrated hydrochloric acid is added. For most precise results, the nitric acid solution should be evaporated to dryness before the hydrochloric acid is added. The results of the determinations are shown in Table III.

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TABLE III

DETERMINATION OF COPPER IN ALLOYS AND ORES

Sample	*No. of Detns.*	*% Cu*	*% Cu Found*	*Std. Dev.*	*% Error*
Al alloy 85	6	4.11	3.9	0.17	−4.9
Al alloy 85A	3	2.48	2.6	0.18	+4.0
Al alloy 86b	9	7.87	8.1	0.37	+3.8
Al alloy 86c	6	7.9	8.6	0.19	+8.9
Brass 37b	11	70.4	70.5	0.92	+0.1
Be bronze PWA3	5	97.5	96.9	1.6	−0.6
Bronze 72	12	91.78	92.6	1.1	+0.9
CBC bronze	12	95.3	95.4	2.3	+0.1
P bronze 63	14	78.1	78.3	0.88	+0.3
Ore 24	6	10.80	11.0	0.85	+1.9
Ore 26	12	10.43	10.7	0.87	+2.8
Ore 29	3	8.98	8.9	0.10	−0.9
Ore 35	9	7.90	8.0	1.1	+1.2
Ore 39	6	6.35	6.4	0.67	+0.8
Ore 45	6	5.85	5.9	0.88	+0.9

DISCUSSION

The fact that the proposed method is of only moderate sensitivity is advantageous because it enables one to determine copper easily in ores and alloys where a more sensitive method would require considerable dilution of the original sample solution. The method is simple and rapid and does not require a hard-to-obtain reagent. The interferences are few and are not difficult to avoid.

While the method is by no means the most accurate for moderate to large amounts of copper, it does give reasonable results and its speed and simplicity should make it suitable for certain types of applications.

SUMMARY

A procedure is proposed whereby copper may be determined spectrophotometrically by means of the very near infrared absorption of its complex ion with hydrochloric acid. Only stannous and ferrous ions are serious interferences and they may be oxidized with nitric acid or with ammonium persulfate to avoid such interference. The method is simple and rapid and is capable of reasonably good precision and accuracy.

RÉSUMÉ

Une méthode de dosage est proposée pour doser spectrophotométriquement le cuivre, par absorption dans le très proche infrarouge, de son complexe avec l'acide chlorhydrique. Seuls les ions stanneux et ferreux gênent réellement. On peut alors les oxyder avec l'acide nitrique et le persulfate d'ammonium. La méthode est simple et rapide, elle présente une suffisamment bonne précision.

ZUSAMMENFASSUNG

Es wird eine Methode vorgeschlagen, um Kupfer spektrophotometrisch zu bestimmen, durch Absorption seines Komplexes in Salzsäure im sehr nahen Infrarot. Nur die Zinn(II) und Eisen(II) Ionen stören wirklich. Man kann sie mit Salpetersäure oder Ammoniumpersulfat oxydieren. Die Methode ist einfach und schnell und bietet eine genügend gute Präzision.

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THE USE OF RHODAMINE B IN ANALYTICAL CHEMISTRY

II. THE DETERMINATION OF SMALL QUANTITIES OF GOLD

by

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During the course of investigations on the determination of antimony with rhodamine B[1] it became evident that under the correct conditions this reagent would be suitable for the determination of trace amounts of gold. The elements likely to interfere, *viz.* antimony, thallium, platinum or vanadium, are all carried down on a manganese dioxide precipitate, whereas the gold is left in solution and could itself be coprecipitated on tellurium according to standard procedure.[2]

In the case of antimony the difficulty of ensuring that all the element is present in the highest valency state has been one of the main obstacles to the development of a method. But with gold, since the auric compounds are more stable than the aurous, no such difficulty was anticipated; also it appeared likely that oxidation prior to the addition of the rhodamine would be unnecessary, and this in fact is correct. However, the method for gold was found to be critically dependent on the amount of hydrochloric acid present and reproducibility was only obtained over a small concentration range.

EXPERIMENTAL

Early experiments in which the technique already developed for antimony was used for the determination of gold, both with and without the oxidation stage, confirmed that oxidation prior to colour development was unnecessary. The method, however, did not give as high a sensitivity as was predicted nor was the reproducibility satisfactory. Further investigation showed that the trouble was due to a combination of two causes, namely, to the difficulty at the extraction stage of obtaining a clean separation of the benzene layer which always appeared cloudy, and to the fact that the colour development proved more sensitive to small changes in chloride and concentration than had been anticipated.

The early experiments had given some indication that the amount of hydrochloric acid present during the colour development might be important in obtaining reproducible results. Accordingly, experiments were carried out to determine the effect of variation in hydrochloric acid and chloride concentrations. In the first case the absorbancy of the rhodamine B complex for a given quantity (25 μg) of gold was determined as before but the concentration of hydrochloric acid was varied. The results showed that the amount of complex formed falls off rapidly with increasing hydrochloric acid concentration. A plot of absorbancy against hydrochloric acid concentration is shown in Fig. 1. It is clear from this graph that for maximum sensitivity not only must the hydrochloric acid concentration be closely controlled but it must be maintained at a low level. To show that the effect of hydrochloric acid was not due to increase of chloride ion, the experiment was repeated with a fixed concentration of hydrochloric acid, but with varying amounts of chloride ion (added as ammonium chloride). The results which are shown in Fig. 2 indicate that chloride also has an effect but the graph indicates that it is of rather a different nature to that of the acid; in any case no serious loss of complex takes place below a chloride concentration of about $2M$.

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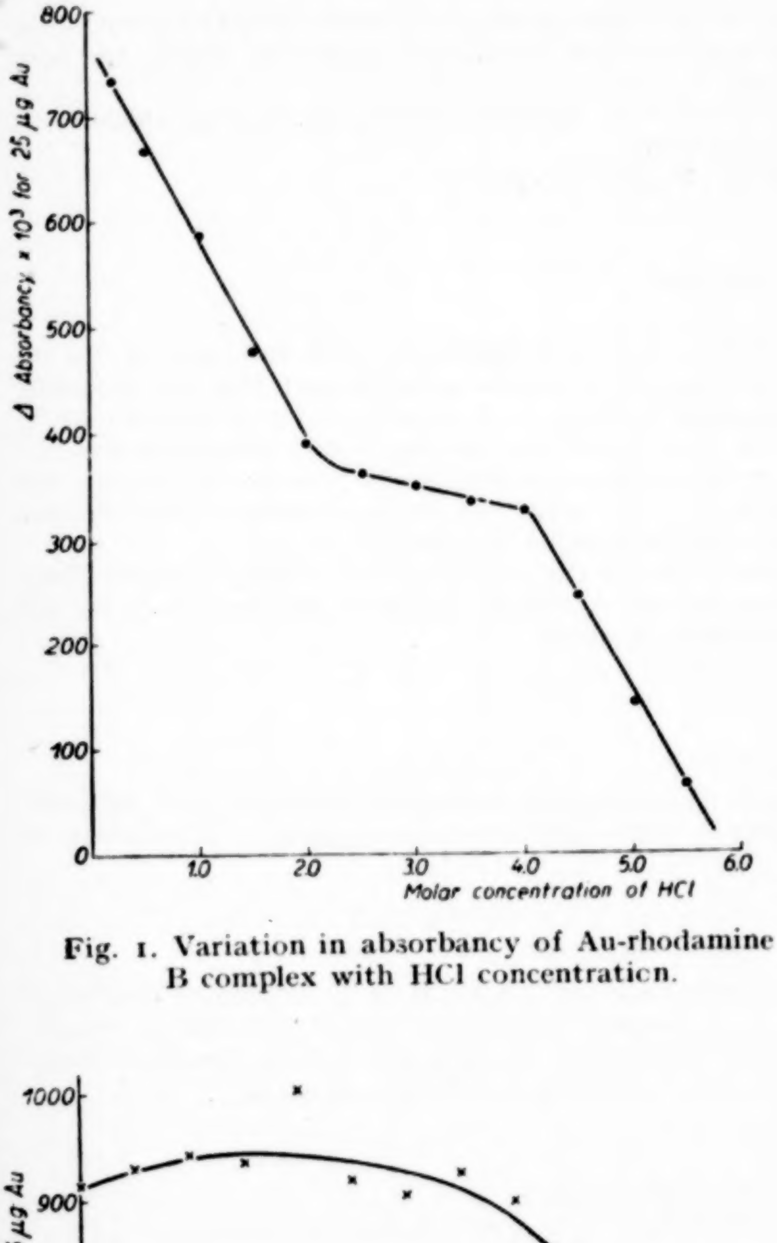

Fig. 1. Variation in absorbancy of Au-rhodamine B complex with HCl concentration.

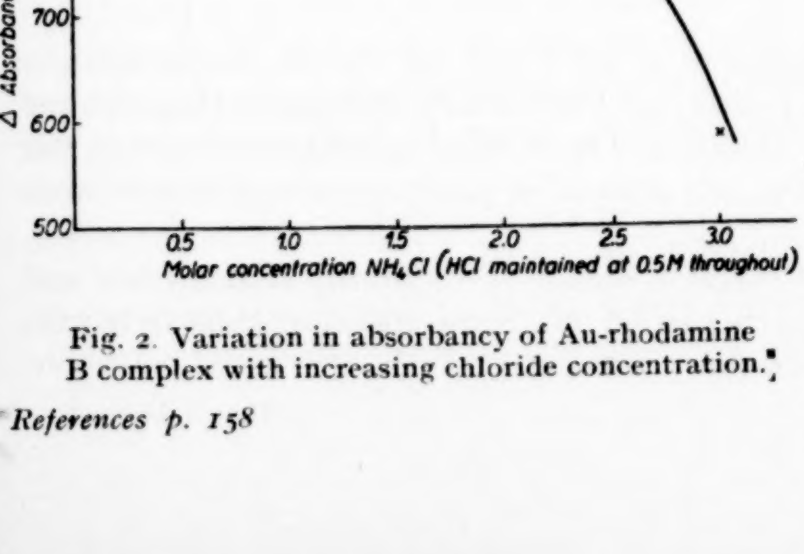

Fig. 2. Variation in absorbancy of Au-rhodamine B complex with increasing chloride concentration.

The method was therefore modified to keep the hydrochloric acid controlled at $0.5M$ and this resulted in more reproducible results than had been obtained previously. Trouble was still met with in the separation of the benzene layer which often appeared cloudy. Attempts to improve the separation of the water and benzene layers by addition of sulphuric acid, phosphoric acid and ammonium salts (chloride sulphate or acetate) failed to improve either the separation or the clarity of the benzene extract. The substitution of *iso*propyl ether for benzene as the extracting liquid overcame this difficulty and provided a clear, readily separable extract. This final modification resulted in a satisfactory method for determining gold with rhodamine B.

Reagents

Standard gold solution. 10 μg/ml. Dissolve 100 mg of pure gold in a few drops of aqua regia in a small covered beaker. Gently evaporate the solution to dryness on a hot plate set at low. Take up the residue in 0.5 ml of aqua regia and make up to 1 litre. This solution (100 μg/ml) is diluted ten times for use.

0.04 % *Rhodamine B solution.* Dissolve 200 mg rhodamine B in a little distilled water and make up to 500 ml.

Constant boiling hydrochloric acid solution. (5 *ca. M.*) Mix 250 ml of 'AnalaR' quality hydrochloric acid and 250 ml of distilled water and distil from a simple distillation apparatus. Reject the first 50 ml of distillate and collect the next 400 ml.

Saturated ammonium chloride solution. Dissolve 150 g 'AnalaR' quality ammonium chloride in boiling water and make up to 500 ml with cold water.

Isopropyl ether. The purest material available should be used.

METHOD

Into a 100 ml beaker pipette 2.5 ml of constant boiling hydrochloric acid, followed by 5.0 ml saturated ammonium chloride solution. Add an amount of sample solution such that the quantity of gold contained therein lies between 0 and 30 μg and make up to 15 ml with water. Add 5 ml 0.04 % rhodamine B solution and transfer the solution to a 75 ml pear shaped funnel containing exactly 10 ml *iso*propyl ether. Shake vigorously one hundred times. Allow layers to separate, discard the aqueous and transfer the ether layer to a corked 6″ × ½″ test tube. Using a Spekker Photoelectric Absorptiometer with Ilford 605 filters measure the absorbancy as follows: —

Set the drum to 1.000 and zero the instrument with a 1 cm cell filled with *iso*propyl ether. Place the ether extract of gold-rhodamine complex in the cell and record the drum reading. Read off the amount of gold present by reference to the calibration graph.

Preparation of calibration graph

To a series of seven beakers numbered 1-7 add 2.5 ml constant boiling hydrochloric acid, followed by 5.0 ml saturated ammonium chloride solution. Then add standard 10 μg/ml gold solution as follows: —

Beaker No.	1	2	3	4	5	6	7
ml of gold solution	0	0.5	1.0	1.5	2.0	2.5	3.0

Make up the total volume of solution to 15 ml in each case; add 5 ml of 0.04 % rhodamine B solution to each and transfer in turn to a 75 ml pear shaped separating funnel containing exactly 10 ml *iso*propyl ether. Extract and measure the absorbancy of each solution as described under Method. Plot the change of absorbancy (*i.e.* 1.000 — reading obtained) against μg of gold.

RESULTS AND DISCUSSION

The results of a series of determination of gold in dilute aqua regia solution, and in dilute aqua regia after coprecipitation on tellurium according to standard technique[3], are shown in Table I.

These figures show satisfactory recoveries of gold and the results are at least as favourable as the best shown by the *p*-dimethyl benzylidene rhodamine reagent[2], and at least double the sensitivity can be obtained. The method as written is suitable for quantities of gold from 0 to 30 μg, but adjustment of quantities should enable much larger amounts to be determined.

It is essential that the quantities of reagents should be vigorously standardized and that the procedure given should be exactly carried out. Some operators seem to require two or three attempts before mastering the technique.

TABLE I

RECOVERY OF GOLD (μg) FROM DILUTE AQUA REGIA (column 2) AND FROM DILUTE AQUA REGIA AFTER COPRECIPITATION WITH TELLURIUM (column 3)

Col. 1 *Added*	*Col. 2* *Recovered*	*Col. 3* *Recovered*
4	3.2	
	3.4	
6	5.5	
	5.6	
	5.4	
	5.7	
	5.7	
	5.7	
8	7.2	
	8.5	
10	8.8	10.0
	9.5	9.8
	10.1	
	8.6	
	8.6	
	8.6	
15	15.2	
	15.3	
	13.4	
	14.0	
20	20.0	19.3
	18.4	19.5
25	25.3	
	26.7	
	24.8	
	25.0	
	25.1	
30	-	28.3
		28.5

The variation of absorbancy of the gold rhodamine complex with pH (*cf.* Fig. 1) provides some grounds for carrying out the determination in about $2.5M$ HCl, which would minimize the effect of small changes of hydrochloric acid concentration. However, owing to the chloride effect (*cf.* Fig. 2) being important here and the loss of sensitivity that would be involved, it is not considered to be worth while. Although this dependence of the method on exact concentration of acid and chloride, which was found when benzene extraction was used, has not been checked separately with *iso*propyl ether as the extracting solvent, it is not expected that this change will have produced any marked effect.

The use of the rhodamine B reagent for the determination of thallium has been investigated so far without success, the difficulty in developing a method in this case arising from the instability of the higher valency compounds of thallium. As yet no oxidizing agent has been found that will consistently retain thallium in a higher

valency state until the complex with rhodamine B is formed and extracted. Once formed and extracted the thallium complex appears to be reasonably stable.

It is hoped ultimately that the investigation of these metal rhodamine B complexes will lead to the complete elucidation of the structure and mechanism of formation.

ACKNOWLEDGEMENT

The authors have to thank MR. A. S. NICKELSON for his interest and encouragement and the Chief Scientist, British Ministry of Supply for permission to publish this paper.

SUMMARY

Using the technique already developed for determination of antimony with rhodamine B a method has been derived for determining small quantities of gold in the range 0-30 μg. Owing to the stability of the higher valency of gold no oxidation stage is required; extraction of the complex is only satisfactory with *iso*propyl ether in contrast with the case of antimony which gives good results with benzene as well as the *iso*propyl ether.

RÉSUMÉ

Utilisant la technique déjà proposée pour le dosage de l'antimoine avec la rhodamine B, une méthode a été établie pour doser de faibles quantités d'or (0 à 30μg). En raison de la stabilité de l'or (III) aucun autre degré d'oxydation n'est nécessaire; l'extraction du complexe n'est satisfaisante qu'avec l'éther *iso*propylique, contrairement à celle du complexe de l'antimoine, donnant de bons résultats aussi bien avec le benzène qu'avec l'éther *iso*propylique.

ZUSAMMENFASSUNG

In Anwendung der schon vorgeschlagenen Technik für die Bestimmung von Antimon mit Rhodamin B wurde eine Methode festgesetzt, um schwache Quantitäten von Gold (0-30 μg) zu bestimmen. Auf Grund der Stabilität des Goldes(III), ist kein anderer Oxydationsgrad notwendig. Die Extraktion des Komplexes ist nur befriedigend mit *iso*propyläther, im Gegensatz zu derjenigen des Komplexes mit Antimon, welche gute Resultate, liefert sowohl mit Benzol als auch mit *iso*propyläther.

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PHOTOMETRIC DETERMINATION OF GALLIUM WITH RHODAMINE B

by

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It is well known that antimony(V), thallium(III), gold(III), and iron(III) react with rhodamine B in hydrochloric acid solution to give red or violet compounds of the type $(RH)M^{III}Cl_4$, which can be extracted by suitable solvents such as benzene. Gallium has recently been found to behave in the same way[1]. We have the general rule that metals giving chloro acids easily extractable by diethyl or *iso*propyl ether react sensitively with rhodamine B. This reaction, in conjunction with the ether extraction of gallium for its separation, provides a rapid and sensitive, as well as specific, method for the determination of traces of this element. The present useful methods for traces of gallium are fluorimetric[2,3]. The proposed procedure can be carried out either absorptiometrically or fluorimetrically, since the benzene solution of rhodamine B chlorogallate is both strongly colored and strongly fluorescent.

The optimum hydrochloric acid concentration for the extraction of rhodamine B chlorogallate by benzene is close to 6.0*M* (Fig. 1). The extractability increases with the rhodamine B concentration but does not reach a constant value at reasonable practical

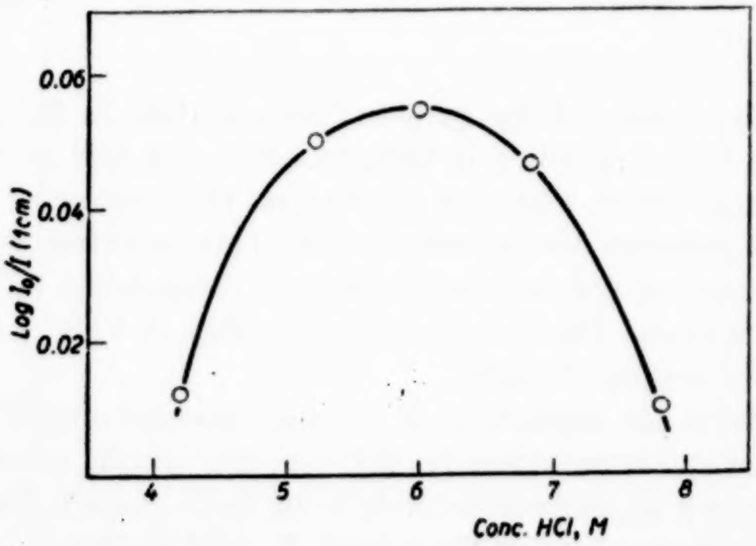

Fig. 1. Extractability of rhodamine B chlorogallate with benzene as a function of the hydrochloric acid concentration. Aqueous phase (5.5 ml) 0.00076*M* (0.036%) in rhodamine B; 10 ml benzene; 2 γ Ga. 1 cm cell, 550 mμ filter (Leitz-Rouy photometer).

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concentrations of the dye (Fig. 2). The extraction coefficient for 6.0M hydrochloric acid and 0.036% (0.00076M) rhodamine B in the aqueous phase is

$$\frac{[\text{Ga}]_{\text{benzene}}}{[\text{Ga}]_{\text{H}_2\text{O}}} = 0.57 \text{ (from Table I)}$$

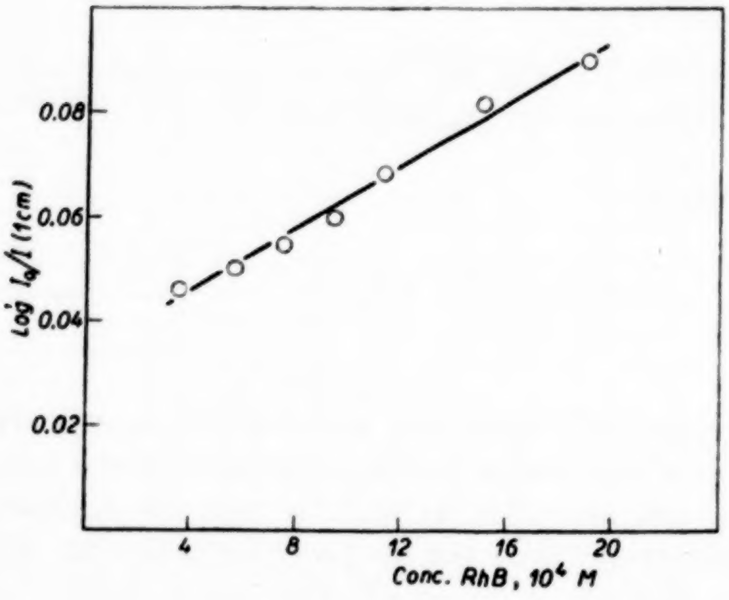

Fig. 2. Extractability of rhodamine B chlorogallate as a function of rhodamine B concentration. Aqueous phase (5.5 ml) 6.0M in hydrochloric acid; 10 ml benzene; 2.0 γ Ga. 1 cm cell; 550 mμ filter.

TABLE I

EXTRACTABILITY OF RHODAMINE B CHLOROGALLATE WITH BENZENE

(Aqueous phase 6.0M in HCl and 0.00076M (0.036%) in rhodamine B; 10.0 ml benzene, 5.5 ml aqueous phase; temperature 24-30° C.)

Ga present, γ	1.0	2.0	3.0	4.0	5.0	6.0	7.0
Extinction of first extract (550 mμ filter)	0.027	0.052	0.082	0.109	0.135	0.163	0.191
Extinction of second (10 ml) extract	0.013	0.024	0.042	0.051	0.067	0.084	0.097
Extraction coefficient*	0.59	0.66	0.60	0.60	0.57	0.53	0.55

* Weighted average is 0.57.

This constant is independent of the gallium concentration in the range investigated. Since, under the conditions specified in the procedure, one-half or more of the gallium remains in the aqueous phase after the extraction, the volume of the aqueous phase must be maintained constant for reproducibility. This condition is easily fulfilled because the ether extract of the isolated gallium is evaporated to dryness before the final determination is made. The standardization curves in Figs. 4 and 5 show that reproducible results are readily obtained.

The absorbance curve for rhodamine B chlorogallate in benzene is given in Fig. 3. At the absorption peak, approximately 565 mμ, the molar extinction coefficient is about 60,000, or 0.0012 γ Ga/cm^2 corresponds to log $Io/I = 0.001$. This may be compared with the value of about 100,000 for rhodamine B chloroantimonate at the same wave length (its maximum lies at 564 mμ). However, since part of the gallium remains in the aqueous phase after extraction, the practical sensitivity is less than indicated by the figure given. When the aqueous and benzene phases are equal in volume, the sensitivity at 565 mμ corresponds to 0.0016 γ Ga/cm² for log I /I = 0.001; when the volume ratio is $\frac{\text{2 benzene}}{\text{1 aqueous}}$ the sensitivity corresponds to 0.0022 γ Ga/cm² for log I_0/I = 0.001, based on the original amount of gallium in the aqueous phase. These sensitivities are exceeded in but few color reactions. When a filter photometer is used in place of a spectrophotometer, the sensitivity will be reduced somewhat depending upon the filter.

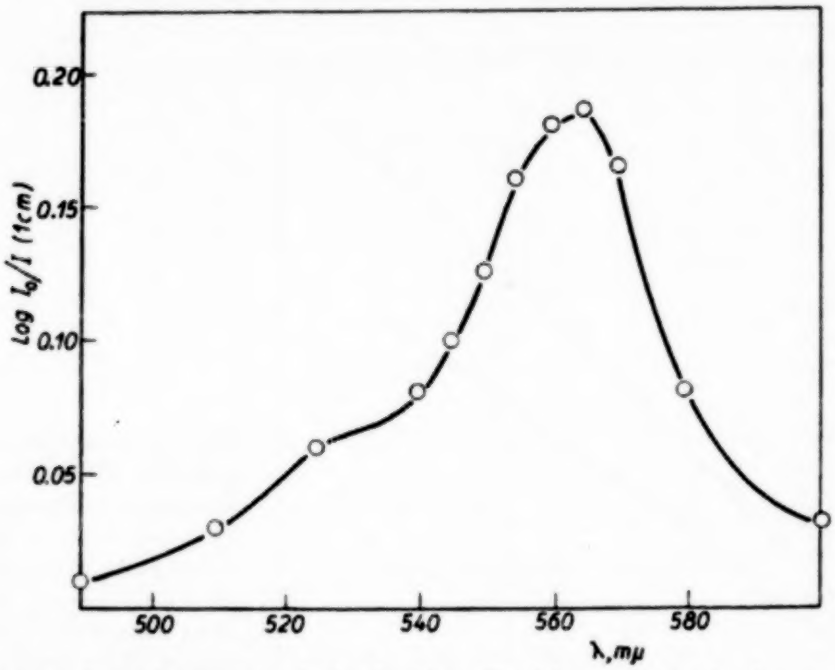

Fig. 3. Extinction-wave length curve of rhodamine B chlorogallate in benzene (0.23 p.p.m. Ga in benzene). Beckman model B spectrophotometer, 1 cm cell. Blank = 0.010.

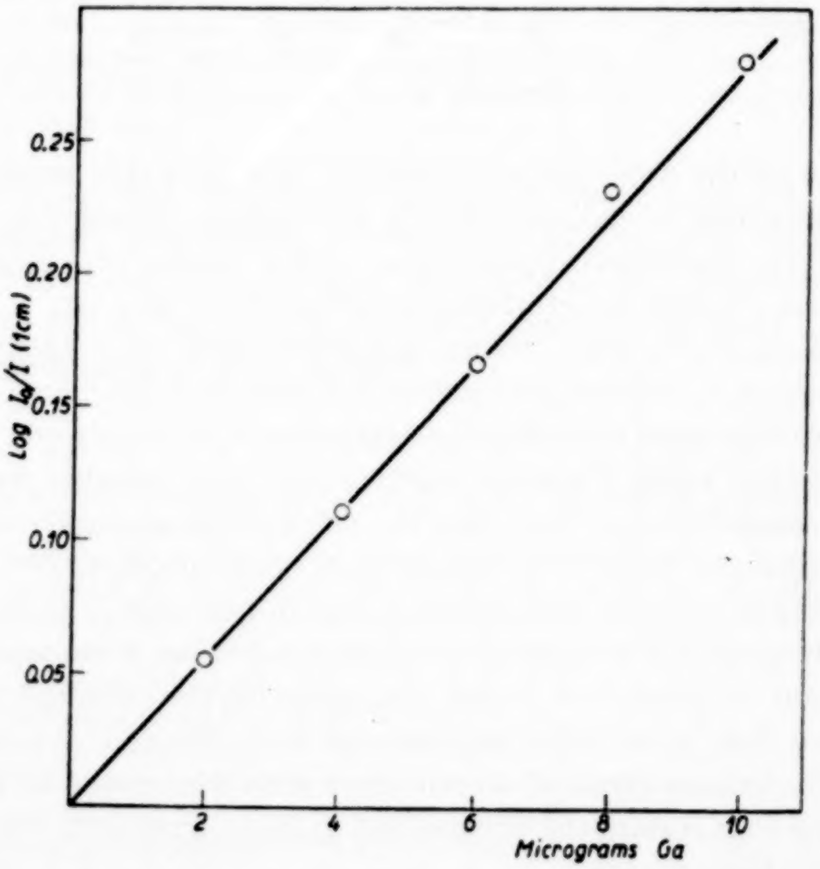

Fig. 4. Extinction curve for determination of gallium by benzene extraction of rhodamine B chlorogallate. 10.0 ml benzene, 5.5 ml aqueous phase; 550 mμ filter, 1 cm cell. The amount of gallium is that present originally in the aqueous phase. A blank reading of 0.009 has been subtracted.

With the filter photometer used in the present work (Fig. 4) the sensitivity was 0.0035 γ Ga/cm^2 for log $I_0/I = 0.001$, when the volume of benzene was double that of the aqueous phase. If the volume of benzene is 10 ml and a 1 cm absorption cell is employed, and the photometric error is assumed to be $\pm$ 0.001 in log I_0/I ($\sim$ 0.2% in transmission) for low extinction values, the error in gallium (in 5 ml of aqueous phase) will be 0.035 γ or say $\sim$0.05 γ. The scatter in the points of Fig. 4 does not much exceed this value.

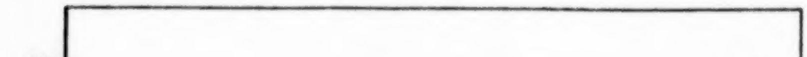

Fig. 5. Fluorimetric determination of gallium by benzene extraction of rhodamine B chlorogallate. Aqueous phase (5.5 ml) 6M in hydrochloric acid and 0.00076M (0.036%) in rhodamine B; 10 ml benzene. Amount of gallium is that originally present in the aqueous phase. The two curves represent measurements at two different sensitivities. Coleman electronic photofluorometer 12 B with filters F_1 = 12-222 and F_2 = PC-2. A blank reading of 7 has been subtracted for Curve A, and of 2 for Curve B.

The sensitivity of the absorptimetric method will probably suffice for the majority of trace determinations of gallium. When the highest sensitivity is required, resort can be made to the fluorimetric procedure. A few tenths of a microgram of gallium in 5 ml of aqueous solution is determinable within 10% (Fig. 5).

Elements such as aluminium, indium, antimony (III), zinc, copper and thallium (I) do not impart a color to the benzene extract[1]. Ferric iron interferes by color formation. Gallium is readily separated from iron by extraction with *iso*propyl ether after reduction of iron to the ferrous state. Titanous chloride is a very suitable reducing agent[4]. Any traces of iron accompanying gallium into the ether phase are easily removed by washing the latter with titanous chloride in hydrochloric acid solution. For *iso*propyl ether the extraction coefficient of gallium from 7M hydrochloric acid is about 200 (50 from 6M, and 100 from 8M acid),[5] as compared to 17 for ethyl ether at the optimum hydrochloric acid concentration of about 6M. Ether extraction in the presence of titanous chloride separates gallium from most other elements as well. The few (*e.g.* germanium and tin) which are more or less coextracted do not react with rhodamine B. The ether extraction also makes it easy to maintain the volume and acidity constant in the benzene extraction of rhodamine B chlorogallate.

Table II lists the results obtained in a test of the proposed method. Especially because as much as 100 mg of iron causes no difficulties, the method should be of quite general applicability. Special cases, *e.g.* those in which metals or their compounds precipitated by titanous chloride are present in large amounts, have not been investigated in the present work.

TABLE II

DETERMINATION OF GALLIUM WITH RHODAMINE B AFTER *ISO*PROPYL ETHER EXTRACTION

(5.5 ml aqueous phase, 10 ml benzene)

Addition	*Ga present, γ**	*Ga found, γ*
none	1.0	1.0
none	2.0	2.2, 2.2, 2.0, 2.1
none	3.0	3.2
none	4.0	3.8
none	5.0	5.0, 4.8
none	7.0	7.3, 7.2
none	10.0	10.2
100 mg Fe(III)	2.9	3.0, 3.0
100 mg Fe(III)	4.9	4.8, 4.8
100 mg Fe(III)	5.9	5.7
100 mg Fe(III)	7.9	7.9, 7.4
0.5 mg Sb(III), 0.1 mg Au(III)	5.0	5.3, 4.6, 5.1
0.5 mg Tl(III)	5.2	5.4, 5.4
40 mg Al	5.0	5.1
1 mg In	5.0	4.8
10 mg Zn, 1 mg Hg(II)	5.0	5.1
10 mg Sn(II), 1 mg Ge(IV)	5.0	5.0
10 mg P(as Na_2HPO_4), 1 mg As(III)	5.1	5.1
1 mg V(V)	5.0	5.1
10 mg Cu(II), 10 mg Ni	5.1	4.9
1 mg Mo(VI), 1 mg W(VI)	5.0	5.0

* Includes Ga in blank: 0.0 γ with no addition, and with Sb + Au, Al, In, Zn + Hg, Sn + Ge, V, and Mo + W; 0.1 γ Ga with P + As and Cu + Ni; 0.2 γ with Tl (the same after double ether extraction); and 0.9 γ with Fe.

The procedure was applied to a granite composite by decomposing a 0.25 g sample with hydrofluoric-sulfuric acid, driving off the excess sulfuric acid, taking up the residue in 7*M* hydrochloric acid and proceeding as described below. Two determinations gave the values 15 and 16 p.p.m. Ga, compared to 17 p.p.m. Ga obtained in earlier work by the fluorimetric 8-hydroxyquinoline method[2].

SOLUTIONS

Titanous chloride (hydrochloric acid solution), 20%. Wash twice with one-third its volume of *iso*-propyl ether to remove traces of gallium.

Isopropyl ether, reagent grade, peroxide-free. Treat as follows daily. In a separatory funnel shake 100 ml of ether with 10 ml of 2% potassium permanganate solution in 2*N* sulfuric acid and drain off the latter. Repeat three times. Add 10 ml of sulfurous acid and shake. After draining off the aqueous phase, wash the ether phase three times with water, and finally with 50 ml of 1:1 HCl

Sodium chloride, 10 g in 100 ml of water.

Hydroxylamine hydrochloride, 10 g in 100 ml of water.

Rhodamine B hydrochloride, 0.50 g in 100 ml of 1:1 HCl.

Standard gallium solution. A convenient concentration is 10 γ of Ga per ml. The solution should be 6*M* in hydrochloric acid. It is stable for at least two weeks.

PROCEDURE

Transfer the solution of the sample (0.5-10 γ Ga in a volume of 5-10 ml), which should be 7*M* in hydrochloric acid, to a separatory funnel and add 2 ml of titanous chloride solution. If the amount of ferric iron exceeds 100 mg, increase the amount of titanous chloride correspondingly. After about 5 minutes shake the solution for 20-30 seconds with 8-10 ml of *iso*propyl ether. When the layers have separated, drain the aqueous phase into another separatory funnel (rinsed with 1:1 hydrochloric acid) and shake with 5 ml of ether. Drain off and discard the acid layer and combine the second ether extract with the first, rinsing the funnel with 1 ml of ether. Separate any small amount of aqueous solution present and shake the ether for 10 seconds with a mixture of 1 ml of $7M$ hydrochloric acid and 0.5 ml of titanous chloride. Drain off the aqueous layer as sharply as possible and shake the ether again with another portion of hydrochloric acid-titanous chloride solution of the same volume. Discard the aqueous washings. Add 1 ml of $7M$ hydrochloric acid to the funnel, shake gently and discard the aqueous solution.

Run the ether into a 50-ml beaker, rinse the separatory funnel with 1-2 ml of ether, add 0.3 ml of sodium chloride solution, cover loosely with a watch glass, and evaporate the ether. (If the ether is turbid from substances precipitated by titanous chloride, filter it through a small plug of glass wool in a small funnel.) Cool, dissolve the residue in 5.0 ml of $6M$ hydrochloric acid and transfer as completely as possible* to a dry separatory funnel. Add 0.40 ml of rhodamine B solution and 0.1 ml of hydroxylamine hydrochloride solution and mix. Add 10.0 (or 5.0) ml of benzene and shake for 1 minute. Allow to stand for a few minutes and drain off the aqueous phase and a small amount of the benzene layer. Filter the benzene extract through a small plug of glass wool in a small funnel to remove water droplets and reject the first portion of the filtrate.

Obtain the transmittancy of the clear solution at 565 mμ. Establish the standard curve by taking, for example, 0, 2, 4, 7, and 10 γ of gallium, adjusting the volume to 5.0 ml in $6M$ hydrochloric acid and proceeding as described above.

Run a blank through the entire procedure.

SUMMARY

Gallium is extractable as rhodamine B chlorogallate with benzene from $6M$ hydrochloric acid, and can be determined absorptiometrically or fluorimetrically in the extract. The interference of iron(III) is avoided by first separating gallium by extraction with *iso*propyl ether from hydrochloric acid solution containing titanous chloride. Traces of gallium can be determined in the presence of aluminium, indium, zinc, antimony, thallium, tungsten and other elements.

RÉSUMÉ

Le gallium peut être extrait comme rhodamine B-chlorogallate en solution chlorhydrique (HCl $6M$) par le benzène. Il peut alors être dosé absorptiométriquement ou fluorimétriquement. La perturbation du fer(III) est empêchée par séparation préalable du gallium, par extraction au moyen d'éther *iso*propylique, de solutions chlorhydriques renfermant du chlorure de titane(III). Des traces de gallium peuvent être dosées en présence d'aluminium, d'indium, de zinc, d'antimoine, de thallium, de tungstène, *etc.*

ZUSAMMENFASSUNG

Das Gallium kann mit Benzol als Rhodamin-B-Chlorogallat ausgezogen werden in salzsaurer Lösung (HCl $6M$). Es kann dann absorptiometrisch oder fluorimetrisch bestimmt werden. Die störende Wirkung des Eisen (III) wird verhindert, indem man es vorher vom Gallium abtrennt durch eine Extraktion mit Hilfe von *Iso*propyläther aus salzsauren Lösungen, welche Titan (III)-Chlorid enthalten. Spuren von Gallium können bestimmt werden in Anwesenheit von Aluminium, Indium, Zink, Antimon, Thallium, Wolfram, *etc.*

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* If 0.1 ml of aqueous solution remains in the beaker, the error in gallium found with 10 ml of benzene for extraction will be 1%, and with 5 ml of benzene about 0.3%.

INORGANIC SALTS IN NON-AQUEOUS SOLVENTS

I. ABSORPTION SPECTRA OF TRANSITION METAL SALTS IN DIMETHYLFORMAMIDE

by

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INTRODUCTION

The absorption spectra of colored metal ions in aqueous solutions have been carefully determined by numerous investigators. Usually, the spectra are characterized by low molar absorptivities which renders it impossible to determine accurately the concentrations of such solutions by spectrophotometric measurements. When the water molecules occupying the coordination sphere of the metal ion are replaced by other ligands, the absorption spectra of the resulting complexes usually differ considerably from the spectra of the hydrated ions. Quite often such change involves a considerable increase in the absorbancy. Such reactions are used extensively in various colorimetric analytical techniques.

Because of the slight solubility of inorganic salts in most non-aqueous solvents, relatively little attention has been paid in the past to the study of such solutions. In particular, little work has been done on the absorption spectra of metallic salts in solvents other than water. Investigations of KATZIN[1] and his co-workers on the absorption spectra of cobaltous salts in alcohol and in acetone, as well as in the mixtures of these solvents with water, have shown that the absorption spectra of the metal ions undergo a profound change as the water molecules of the coordination sphere are replaced progressively by the molecules of organic solvent.

Recent work on the properties of dimethylformamide has brought to light its ability to easily dissolve a number of inorganic salts. This property was subsequently utilized in a spectrophotometric determination of copper as the 2,2′-biquinoline complex in 50% dimethylformamide[2]. It was noticed in the course of this investigation that the absorption spectrum of copper salts in the dimethylformamide was radically different from the spectra of the aqueous solutions of these salts. The absorption peak was shifted to the shorter wavelengths and the absorbance of the solutions is much higher than in water. The absorption spectrum of the 2,2′-biquinoline copper(I) complex in dimethylformamide likewise showed a considerable increase in the molar absorptivity, although there was no change in the position of the maximum.

Since most metallic salts are soluble in dimethylformamide and since they apparently retain their ability to react with chelating agents, it is quite probable that analytical determinations of other metals besides copper can be rendered more sensitive by the use of this solvent. It was decided that a detailed investigation of the metal salts-dimethylformamide system should be of considerable interest. The work reported here represents the first phase of the investigation in which a survey is made of the absorption spectra of transition metal salts in dimethylformamide.

EXPERIMENTAL PART

All spectrophotometric measurements were made on a Cary recording spectrophotometer model 11. Stoppered silica cells of pathlength 1.00 ± 0.01 cm were used throughout the investigation. The measurements were made at room temperature of approximately 25°.

Dimethylformamide was obtained from the Rohm and Haas Co. The solvent was purified by drying it with barium oxide for a period of 24 hours and then distilling through a threefoot packed column. The middle fraction boiling at 151 ± 1° at 750 mm was used in subsequent work.

The salts used were chromium(III) acetate, chloride and perchlorate, manganese(II) acetate, cobalt(II) acetate, chloride, nitrate and perchlorate, nickel(II) acetate, chloride, nitrate and perchlorate, copper(II) acetate, chloride, nitrate and perchlorate, iron(II) sulfate and iron(III) chloride, nitrate and perchlorate. All of these salts contained the usual number of water molecules of hydration and were easily soluble in the dimethylformamide at room temperature. They were all of reagent grade quality. Absorption measurements were made in the concentration range of $1.0 \cdot 10^{-1} M$ to $2.0 \cdot 10^{-4} M$. Stock solutions were prepared by dissolving a weighed amount of each salt in a given volume of dimethylformamide. Experimental solutions were prepared by the dilution of the stock solutions.

In order to study the effect of anions on the absorption characteristics of the metal ions, acetate, chloride, nitrate and perchlorate were added in the form of lithium acetate, lithium chloride, sodium nitrate and potassium perchlorate. These salts are relatively soluble in dimethylformamide and their solutions do not absorb in the visible region of the spectrum.

RESULTS AND DISCUSSION

The absorption spectra obtained in this investigation are shown on Figs. 1 through 6. Wavelengths of maximum absorption and the values of the molar absorptivity are given in Table I.

Fig. 1 shows the absorption spectra for the chromium(III) acetate, chloride, and perchlorate. The absorption curves for the acetate salt in water and in dimethylformamide are practically identical. The chloride and perchlorate salts in the organic solvent show some similarities with the greatest variation appearing in the chloride solutions. Molar absorptivities for the salts in the organic medium are appreciably larger than for the corresponding species in an aqueous system.

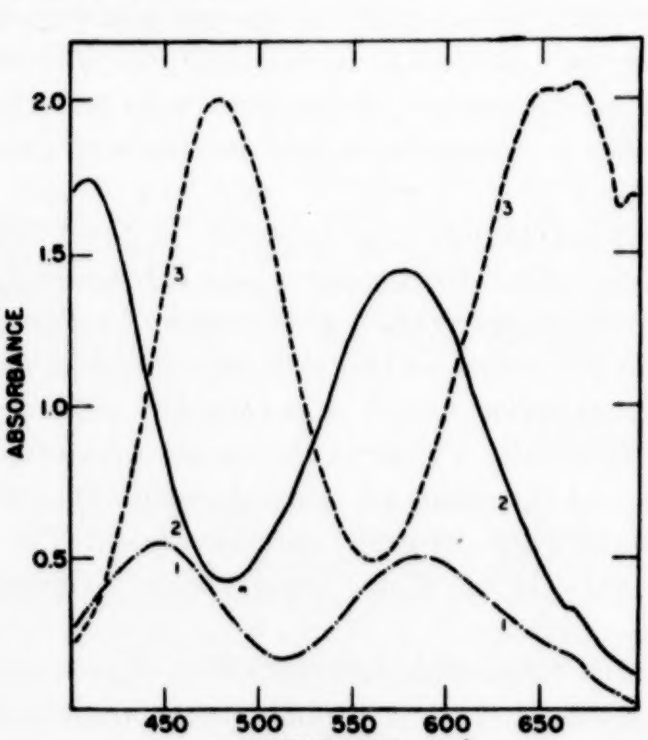

Fig. 1. Absorption spectra of chromium(III) salts in dimethylformamide

1. $Cr(C_2H_3O_2)_3 \cdot 2H_2O$	$1 \cdot 10^{-2} M$
2. $Cr(ClO_4)_2 \cdot 6H_2O$	$1 \cdot 10^{-1} M$
3. $CrCl_3 \cdot 6H_2O$	$4 \cdot 10^{-2} M$

References p. 171

TABLE I

ABSORPTIOMETRIC DATA FOR TRANSITION METAL SALTS IN DIMETHYLFORMAMIDE IN THE VISIBLE REGION OF THE SPECTRUM

Salt	max_1	a_m	max_2	a_m
$Cr(OAc)_3.2H_2O$	450	60	585	55
$CrCl_3.6H_2O$	480	50	670	48
$Cr(ClO_4)_3 \cdot 6H_2O$	410	18	575	16
$Mn(OAc)_2 \cdot 4H_2O$	490	—	—	—
$FeSO_4 \cdot 7H_2O$[a]	315	6500	362	5800
$FeCl_3 \cdot 6H_2O$[a]	315	7150	362	6750
$Co(OAc)_2 \cdot 4H_2O$	540	40	—	—
$CoCl_2.6H_2O$	665	277	—	—
$Co(NO_3)_2 \cdot 6H_2O$	522	22	—	—
$Co(ClO_4)_2 \cdot 6H_2O$	522	18	—	—
$Ni(OAc)_2 \cdot 4H_2O$	400	15	675	5
$NiCl_2.6H_2O$	420	12	620	30
$Ni(NO_3)_2 \cdot 6H_2O$	400	13	670	15
$Ni(ClO_4)_2 \cdot 6H_2O$	400	13	670	5
$Cu(OAc)_2 \cdot H_2O$	700	190	—	—
$CuCl_2 \cdot 2H_2O$	435	160	—	—
$Cu(NO_3)_2 \cdot 6H_2O$	750	30	—	—
$Cu(ClO_4)_2 \cdot 6H_2O$	750	35	—	—

[a] In presence of HCl.

The manganese(II) system is shown in Fig. 2. The spectra obtained with the chloride and the acetate show some interesting changes with time. Solutions change from yellow through red to a deep brown upon standing for a few hours.

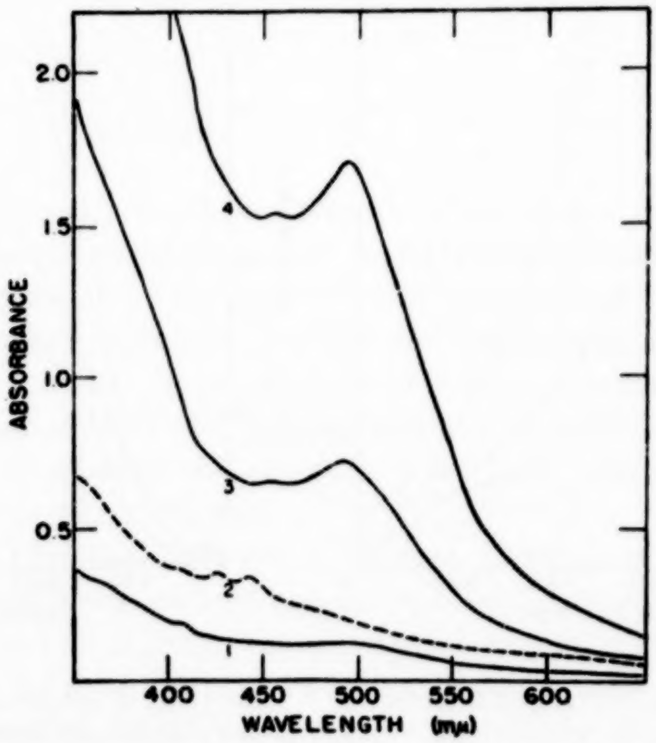

Fig. 2. Absorption spectra of manganese(II) salts in dimethylformamide

1.	$Mn(C_2H_3O_2)_2 \cdot 4H_2O$	$1 \cdot 10^{-1}M$
2.	$MnCl_2 \cdot 4H_2O$	$3 \cdot 10^{-1}M$
3.	$Mn(C_2H_3O_2)_2 \cdot 4H_2O$	(dilution of 1 after 1 hour)
4.	$Mn(C_2H_3O_2)_2 \cdot 4H_2O$	(dilution of 3 after 1 hour)

The solution represented by curve 4 was prepared by a many fold dilution of the original solution (curve 1) after a period of six hours. No precipitates were observed in the solutions even after much longer periods of aging. It is apparent that some type of reaction between the salt and the solvent occurs which renders the system unsuitable for analytical considerations.

Two oxidation states of the iron system were investigated. The absorption curves for the iron(III) salts are shown in Fig. 3. Addition of one drop of concentrated hydrochloric acid to 22 ml of the chloride solution caused a tremendous change in the absorption spectrum. An identical curve was obtained on the addition of acid to an iron(II) chloride solution. The similarities suggest that the same absorbing species exist in the two solutions. It is logical, in view of the reducing nature of the solvent[2], to suppose that the absorption is attributable to an iron(II) species. This was actually shown to be the case by the addition of 1,10- phenanthroline to these systems. In both solutions, the red iron(II)-1,10-phenanthroline complex was formed, and no trace was found of the blue iron(III)-1,10-phenanthroline complex.

Cobalt salts in dimethylformamide present a very interesting subject for investigation. It can be seen from the curves in Fig. 4 that large variations exist in solutions of the the salts. The blue chloride solutions are in marked contrast to the red nitrate and the violet acetate solutions. These variations in absorption characteristics with differences in the anion of the salt are due to coordination tendencies between the metal ion and the solvent and between the metal ion and the particular anion species. As a result,

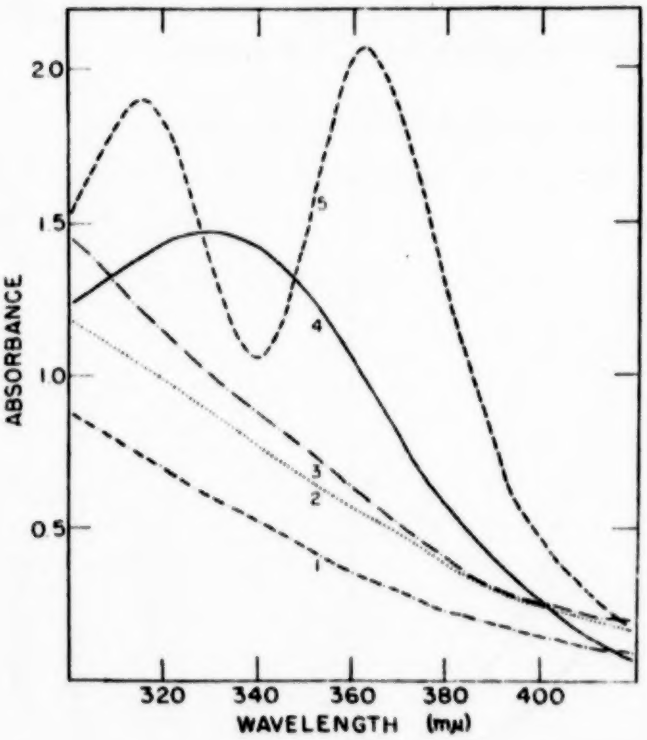

Fig. 3. Absorption spectra of iron(III) salts in dimethylformamide

1. $Fe_2(NO_3)_6 \cdot 9H_2O$ $1.55 \cdot 10^{-4} M$
2. $FeCl_3 \cdot 6H_2O$ $3.7 \cdot 10^{-4} M$
3. $Fe(ClO_4)_3 \cdot 6H_2O$ $5.0 \cdot 10^{-4} M$
4. $Fe_2(NO_3)_6 \cdot 9H_2O$ (with HNO_3) $1.55 \cdot 10^{-4} M$
5. $FeCl_3 \cdot 6H_2O$ (with HCl) $3.0 \cdot 10^{-4} M$

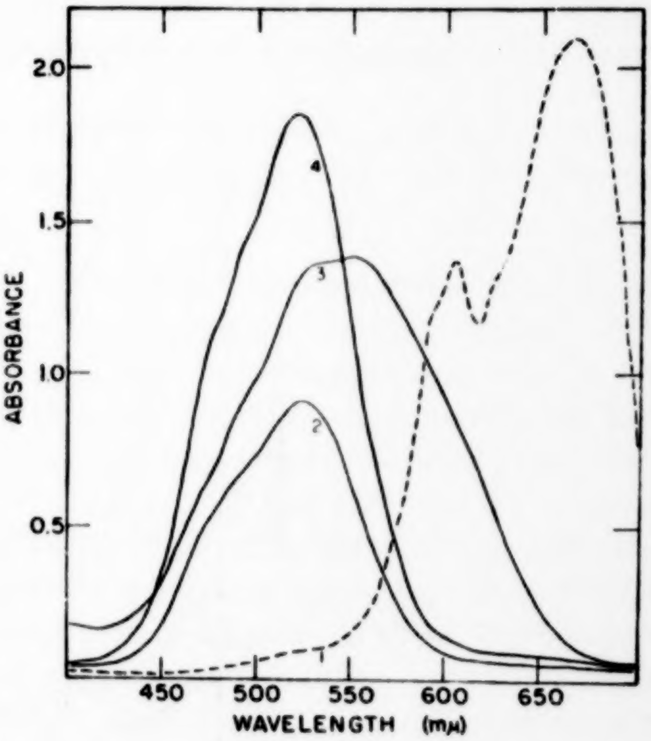

Fig. 4. Absorption spectra of cobalt(II) salts in dimethylformamide

1. $CoCl_2 \cdot 6H_2O$ $7.5 \cdot 10^{-3} M$
2. $Co(NO_3)_2 \cdot 6H_2O$ $4.2 \cdot 10^{-2} M$
3. $Co(C_2H_3O_2)_2 \cdot 4H_2O$ $3.7 \cdot 10^{-2} M$
4. $Co(ClO_4)_2 \cdot 6H_2O$ $1.0 \cdot 10^{-1} M$

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anions that are known to enter most readily into complex formation cause the greatest variations in the absorption spectra.

Nickel and copper salts in dimethylformamide were also studied. Absorption spectra for the nickel solutions are shown in Fig. 5. All of the nickel salts studied dissolve to form green solutions. The chloride system again shows the greatest deviation from the normal spectra observed in aqueous solution.

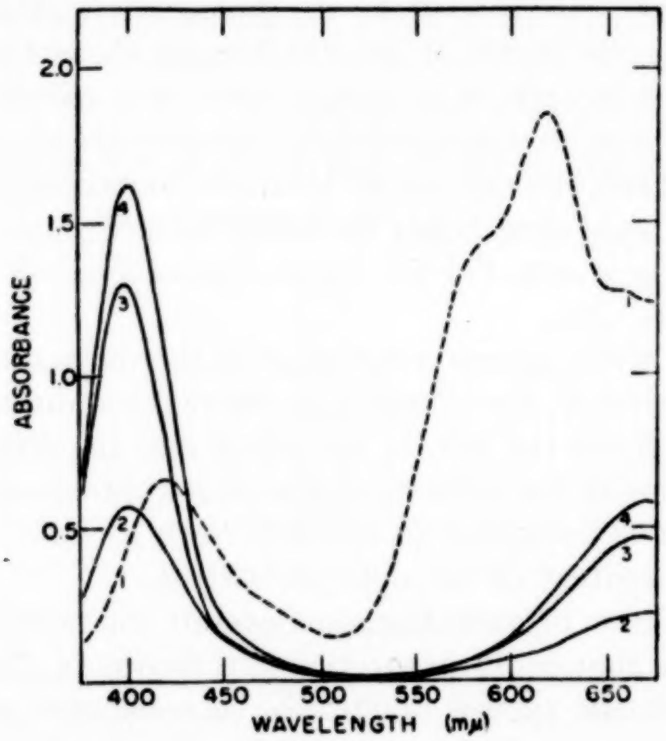

Fig. 5. Absorption spectra of nickel(II) salts in dimethylformamide

1. $NiCl_2.6H_2O$	$5.3 \cdot 10^{-2} M$
2. $Ni(C_2H_3O_2)_2.4H_2O$	$4.0 \cdot 10^{-2} M$
3. $Ni(ClO_4)_2.6H_2O$	$1.0 \cdot 10^{-1} M$
4. $Ni(NO_3)_2.6H_2O$	$1.2 \cdot 10^{-1} M$

Copper salts in dimethylformamide likewise show some interesting phenomena. Only one absorption maximum is apparent at wavelengths longer than 400 mμ. The nitrate shows a maximum at 775 mμ which corresponds approximately to that for the copper(II) ion in aqueous solution. Acetate and perchlorate solutions have maxima at 700 mμ. A chloride solution is emerald green with a maximum at 435 mμ. Thus, the main effect of dissolution in the organic medium is a shift in the wavelength of maximum absorption to shorter wavelengths. This large shift brings the maximum into the visible region of the spectrum.

A study on the effect of the addition of acetate, chloride nitrate, and perchlorate ions to the colored solutions was carried out. In each system, the chloride ion was found to have the greatest effect in altering the absorption characteristics of the metal ions. The order of reactivity, as measured by wavelength shifts, was $Cl > OAc > NO_3 > ClO_4$. This is the order of complex formation tendency as usually assigned to these anions.

In the cobalt system, the addition of lithium chloride to solutions of the acetate, nitrate, and perchlorate salts gives striking results in that the color change is from red or red violet to blue. The color change in dimethylformamide is so complete that cobalt salts in this solvent could serve in the determination of chloride ion. Small amounts of the ion could be determined simply by the addition of a soluble chloride to the cobalt salt. A predetermined calibration curve would permit calculation of chloride concentration.

The cobalt chloride system in dimethylformamide lends itself to the analytical determination of water in substances soluble in the medium. The addition of water to a blue solution of the salt results in a color change to pink. This color change in anhydrous ethanol on the addition of water has been proposed as the basis for the determination of water. The difficulties encountered in the preparation of the ethanolic medium can be circumvented by the choice of dimethylformamide as the solvent medium.

Results on a study of the effects of added water to a cobalt chloride solution are presented in Table II. The study was carried out on a $4 \cdot 10^{-3} M$ solution of cobalt chloride. Values of absorbance at 605 and 665 mμ for solutions containing 0-10% water are listed in the table. Solutions containing larger concentrations of water are pink and the absorbance value at 665 mμ is zero. For the concentration of cobalt salt chosen, the upper limit for added water is 12%.

A plot of percentage water against absorbance at the above stated wavelengths showed a straight line relationship. The absorbance before the addition of any water appears to be low and does not lie on the line. It was found that the difference in the observed absorbance and the value at the ordinate intercept is approximately that which can be attributed to the water of hydration in the salt. Such a result suggests a method for determining the water content of the salts themselves.

The effects of the addition of water to copper acetate solutions were also investigated. Curves representing the changes in absorption are shown in Fig. 6. It is graphically portrayed that water in the system drastically decreases the absorbance. The molar

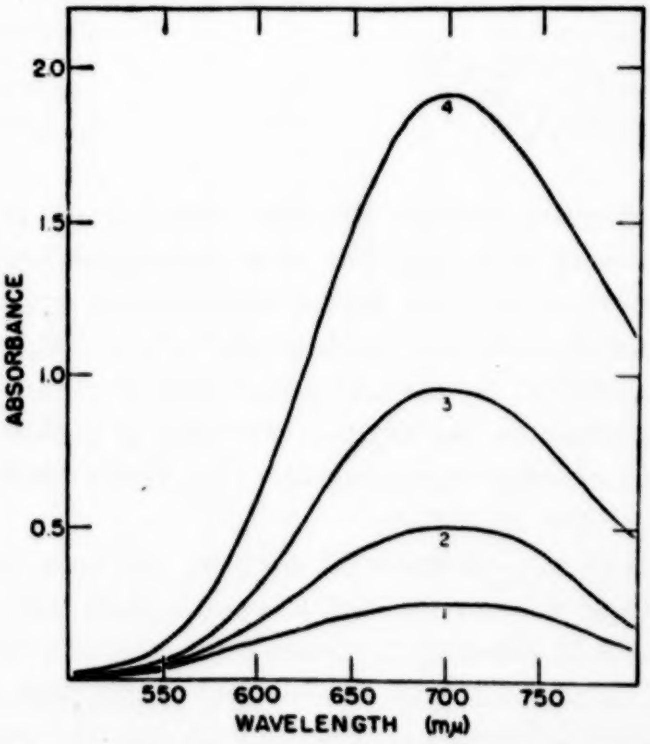

Fig. 6. Effect of water on the absorption spectrum of copper(II) salts in dimethylformamide

1. $Cu(C_2H_3O_2)_2$ $5 \cdot 10^{-3} M$ in DMF (10% H_2O)
2. $Cu(C_2H_3O_2)_2$ $5 \cdot 10^{-3} M$ in DMF (4% H_2O)
3. $Cu(C_2H_3O_2)_2$ $5 \cdot 10^{-3} M$ in DMF
4. $Cu(C_2H_3O_2)_2$ $1 \cdot 10^{-2} M$ in DMF

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absorptivity of the salt in the anhydrous solvent at 700 mμ is 190 as compared to 7 for the copper ion in aqueous solution at the same wavelength. Copper acetate in dimethylformamide has a molar absorptivity that is more than three times larger than that for the copper ammonia complex (190 to 56). These values are observed at the absorption maxima of 700 mμ for the copper salt in dimethylformamide and at 616 mμ for the copper ammonia complex in aqueous solution. It is seen from the above results that the sensitivity of the colorimetric measurement of copper in dimethylformamide compares very favorably with the ammonia method[3].

TABLE II

ABSORBANCE VALUES FOR THE $CoCl_2$-H_2O SYSTEM IN DIMETHYLFORMAMIDE

% H_2O	*Absorbance at 605 mμ*	*Absorbance at 665 mμ*
0	0.57	0.86
2	0.55	0.80
3	0.50	0.73
5	0.38	0.55
6	0.33	0.46
8	0.22	0.28
9	0.16	0.18
10	0.10	0.09

ACKNOWLEDGEMENT

The authors gratefully acknowledge the assistance of J. GERLACH, L. HOWICK, A. OSTROFF AND W. PEARD of this Laboratory in obtaining some of the absorption spectra described in this article.

SUMMARY

Absorption spectra of Cr, Mn, Fe, Co, Ni and Cu salts have been determined in dimethylformamide. In most cases the spectra differed considerably from those in aqueous solutions. The absorption maxima and the molar absorptivities of these salts in dimethylformamide are tabulated. The spectra are strongly influenced by the presence of certain anions, the order of decreasing effect being Cl^-, OAc^-, NO_3^- and ClO_4^-.

RÉSUMÉ

Les spectres d'absorption des sels de Cr, Mn, Fe, Co, Ni et Cu ont été déterminés dans la diméthylformamide. Dans la plupart des cas, les spectres diffèrent de ceux obtenus dans les solutions aqueuses. Les maxima d'absorption et les valeurs d'extinction moléculaire sont donnés. Les spectres sont influencés par l'addition d'anions étrangers, dans l'ordre décroissant suivant: Cl^-, OAc^-, NO_3^-, et ClO_4^-.

ZUSAMMENFASSUNG

Die Absorptionsspektren von den Cr-, Mn-, Fe-, Co-, Ni- und Cu Salzen wurden in Dimethylformamid bestimmt. In den meisten Fällen weichen diese Spektren von denen, die man in wässriger Lösung erhält, ab. Die Absorptionsmaxima und die molekularen Extinktionswerte werden angegeben. Die Spektren werden beeinflusst durch die Zugabe von fremden Anionen, welche in der folgenden Anordnung an Stärke verlieren: Cl^-, OAc^-, NO_3^- und ClO_4^-.

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FUNDAMENTALS OF HETEROMETRY AND THEIR INTERPRETATION

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INTRODUCTION

During our studies of the behaviour and the composition of metal complexes of citrates, tartrates, oxalates, meta- and polyphosphates *etc.*, we endeavoured to find a method for the direct study of the complex compounds in the heterogeneous system. The desired method had to be rapid and based upon physical processes only, presenting the advantages of the classical methods of studying compounds by crystallization, separation and gravimetric determination. In addition to the results which are obtained by the classical method, it was desired to obtain information about the stability and the solubility of the compounds investigated. Contrary to the classical methods which deal with the study of the *final* and most *stable* compounds, we were interested in all the *intermediates* which appear in the system *before* the final compound is formed. The necessary condition was therefore *not* to interfere in any way with the system, in order to enable simultaneous study of the unstable compounds existing during the formation of the final compound.

As the purpose was to investigate the reactions which occur in the heterogeneous system by measuring the changes in light intensities, colour *changes* of the system had to be eliminated. It was hoped to study the colour changes during the process separately by a different method.

We commenced with photometric titrations of homogeneous solutions using colour filters, and attempted to extend these titrations to reactions which take place with the formation of precipitates. The next step was to measure the optical effects of the precipitates separately. With this purpose in mind, we built a "Heterometer" and tried to draw "heterometric curves" of various chemical reactions. The "Heterometer" was specially designed and constructed by us for electrophotometric titrations involving suspensions. The light passed vertically, during the titration, through the cylindrical absorption cell and fell on the photometric cell. The readings on the Galvanometer were made with an accuracy of ± 0.001 microamp and the optical density was calculated to three decimal places. The readings were recorded at 0.1-0.2 ml intervals only after a constant value was obtained, usually after a few seconds to a minute. The usual rate of stirring of the solution was 600 r.p.m. and was generally the maximum consistent with stable measurements. Experiments were repeated after several months to check the reproducibility of the density curves, which, in general, was very good. The maximum optical density values varied somewhat, but the critical points on the horizontal axis remained the same in all cases. During the past five years more than a thousand chemical reactions were studied heterometrically and about twenty thousand heterometric titrations were made.

In this report we present the basic phenomena of *heterometry* with the purpose of giving a more general picture of the scope of problems which may be dealt with heterometrically. This, it seems to us, will help towards a better understanding of investigations which are carried out using this method[1].

In this paper we give a general description and discussion of heterometric phenomena whilst in a special report we shall discuss different chemical reactions on the basis of the heterometric curves drawn for them. From the information obtained we shall evaluate the *general chemical* and *analytical* aspects and applications.

Scope of heterometry

Heterometry deals with the photometric study of chemical reactions in suspensions *on a quantitative basis*. It is concerned both with reactions which occur in the *solution* as well as those in the *solid* state. *Heterometric titration curves* (optical density curves) are obtained and the location of the *critical points* determined. Heterometry deals primarily with *end-points* and is *less* concerned with whether the particles are of unit or varying size. The heterometric determination *does not interfere* with the system studied and is *not* limited to the study of *final* reactions, but also gives information about the *intermediates*. A heterometric curve drawn from a reaction measured under suitably chosen conditions of composition and concentrations, presents a description of the reactions *in all its phases* on a quantitative basis.

Limits of concentrations

The limits of concentrations of the reacting components used in heterometry are very broad. They depend on the solubility and on the stability of the compounds studied in the chosen medium. Many reactions were studied by us in a concentration as high as 0.1 M. For analytical reactions, the molar concentration of the components is generally about $10^{-3}M$ to $10^{-4}M$, and for more sensitive reactions the concentrations lie between $10^{-5}M$ and $10^{-6}M$. The latter is probably the lower limit of concentration which can be studied by heterometry.

Heterometric curves

On titrating a solution A with a solution B, at a certain stage a solid phase will be formed. The system will now be composed of one or more intermediates existing side by side both in the liquid and in the solid state simultaneously. On continuing the titration dropwise, stirring vigorously, structures of greater stability will appear more or less rapidly, in the solid as well as in the liquid states. If such a reaction is studied under well chosen conditions of composition and concentration, following the light intensity which is transmitted through the system, we obtain a *heterometric absorption curve*. (The colour changes, if such do exist, must be eliminated by the use of filters.) These curves give a description of the partial reactions which occur successively in the suspension on a quantitative basis. A heterometric curve is therefore a line with sharp breaks which are the *critical points*. So far no quantitative meaning can be given to the *absolute* optical density values measured at the various points. In contrast, the relative changes of these values, especially near the critical points, are of utmost importance. Fig. 1 presents a series of simple heterometric curves drawn schematically.

A heterometric curve may be obtained in two different ways: the more general way is to draw the curve showing the process of *precipitation*. The curve shows the different stages of the chemical reaction proceeding successively, (see the left parts of the curves of Fig. 1). The second way, the curve may be the result of a gradual dissolution of a fresh precipitate (see the right hand part of the curves of Fig. 1). A curve may be composed of both parts in the case where an insoluble compound is first obtained and is redissolved on the addition of an excess of titrant (see Fig. 1, curves 2, 4, 5, 6 and 8). The heterometric study of the process of *dissolution* is in many cases much more complicated than the study of the process of precipitation, and the shape of the curves which are obtained in both cases may be of a different character. In the case of reaction (1) (see below) a symmetrical curve may be obtained with a maximum optical density point in the middle (Fig. 1, curves 2, 5 or 8). In many other cases, the curve of dissolution is not the reflected image of the curve of precipitation. The dissolution may not occur stoichiometrically and is not completed as expected (Fig. 1, curves 4, 6 and 7). We may explain this by the new conditions which exist in the solid state, by the rearrangement of the material and the formation of particles which are not so easily susceptible to chemical influences. In many cases this process of dissolution can be better studied by the reverse process of precipitation. This is the case if we measure heterometrically the reaction (2) instead of reaction (1). Schematically, we may present both cases as follows:

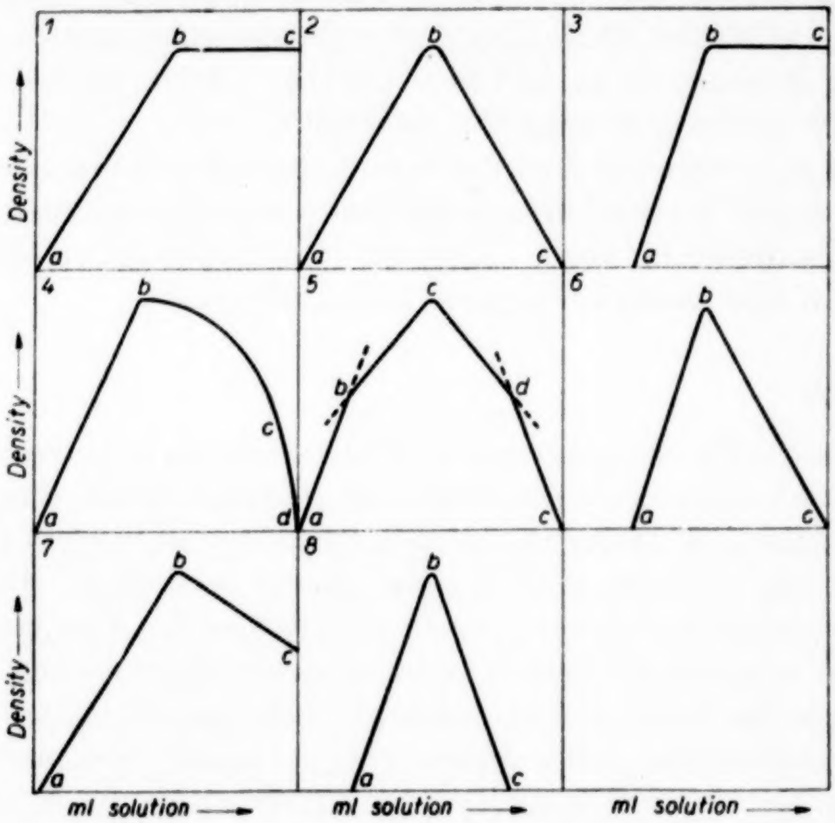

Fig. 1. Heterometric titration curves.

$$A + B \rightarrow AB \downarrow + B \rightarrow AB_2 \uparrow \qquad (1)$$

or

$$2B + A \rightarrow AB_2 \uparrow + A \rightarrow A[AB_2] \downarrow \text{ (or } 2AB \downarrow) \qquad (2)$$

($\downarrow$ = precipitation; $\uparrow$ = solution.)

If the reaction is studied both ways we obtain a deep insight into the character of the intermediates which generally form a kind of a "reaction chain" which terminates with the formation of final and stable materials. The reaction (2) proceeds in the following way (Fig. 1, curves 3 or 8); the substance A is added dropwise to the substance B. At the point "a" the formation of the soluble complex [AB_2] is quantitative. By the further addition of A, an insoluble compound AB is quantitatively formed at point "b". The reaction may stop and on further addition of the titrant a maximum optical density *line* is produced (curve 3). Another possibility is often given in the reaction (3):

$$AB \downarrow + A \rightarrow A_2B \uparrow \qquad (3)$$

The part of dissolution may correspond to the branch "bc" (curve 8), but other possibilities do exist and they are presented schematically in curves 4 (bcd), 5 (cde), 6 (bc) and 7 (bc). Only curve 1 presents a simple precipitation reaction which proceeds quantitatively without complex formation. Reaction (1) leads to a heterometric curve 2. From the beginning ("a") the insoluble AB is precipitated. At point "b" the first part of the reaction (1) is completed. The dissolution is completed in point "c". Altogether we deal in the above cases with *three* critical points only; the point of the ***initial precipitation***, the *first* point of the ***maximum optical density*** and the point of the ***complete dissolution***. The point of the *initial* precipitation may show either the solubility of a compound which is then precipitated or may coincide with the point at which formation of a soluble complex is quantitative. The *first* maximum density point coincides in all cases with the point of complete precipitation of an insoluble compound and is therefore very important for the quantitative micro-determination of cations or anions. Both points mentioned can be used extensively for analytical purposes.

Three final critical points have so far been mentioned, each lying at the end of a reaction and signifying the formation of a stable compound. Heterometric curves which show additional critical points are more complicated but more interesting. Curve 5, Fig. 1 shows such two additional critical points (b and d). Points such as these generally appear when insoluble intermediates are formed, which, on further addition of titrant are transformed into more stable compounds. The interpretation of these more complicated curves requires a clear understanding of the chemical reaction studied, in addition to experience previously gained by studying simpler heterometric curves. Such curves (curve 5 is the most simple) give additional information as to the way in which heterometric reactions proceed and give evidence of the structures of the final compounds which are written in the chemical equations. In another further report on heterometry we shall give many examples of reactions which give such complicated heterometric curves and their interpretation. There is no theoretical limit to the number of critical points which may appear in one heterometric curve. Reactions were studied by us heterometrically in which iron, aluminium and chromium were determined with precision in one titration from the critical points appearing on a single curve.

Heterometry and turbidimetry

Having a concept of the heterometric method, we can interrelate heterometry with other physical methods. Heterometry was not developed until recentlyfor the following reason: the classical colorimetric method of measuring light absorption could not be easily adapted to the study of continuously changing intensities, although in principle this could be done with success equal to that in measuring the light absorption in a Dubosque colorimeter. Unfortunately, the measuring of light absorption through suspensions was identified in the past with a condition *sine qua non*, that the particles of the suspension have to be approximately of unit size. In the measurements that are made under these conditions a linear relation between the quantity of material and the light absorption is found. *This situation, basic to "turbidimetry", is generally not observed in "heterometry"*. No protective colloids are used in heterometry as opposed to turbidimetry. Our experience shows that colloids change the nature of the heterometric curves and as a result the critical points become uncertain. The selection of materials which are suitable for turbidimetric studies is very restricted from the outset and the classical suspensions which are obtained in analytical chemistry are mostly unsuitable for turbidimetric-titrimetric studies. In developing the heterometric method we felt *that particle size was not of prime importance in determining end-points* (critical points) in which we were fundamentally interested.

Heterometry and conductometry

Comparing heterometric and conductometric titrations, we find the following differences: conductometry deals chiefly with reactions which occur in *solution* and gives little or no information of what happens in the solid phase, if such exists. It does not differentiate between a soluble undissociated compound and a precipitate. Conductometric titrations have to be carried out at a concentration in the order of $10^{-2}M$ whilst in heterometric titrations the usual concentration is approximately one hundred times lower. Since conductometry requires that the volume remains nearly constant during the titration, the titrant must be concentrated, thus excluding the use of sparingly soluble compounds as titrants. No such limitations exist in heterometry: the volume may change greatly during the heterometric titration and even an increase of 30 % in volume does not affect the results if a sufficiently insoluble compound is studied. The critical points appear, in all cases, at the calculated end-points and only the absolute optical density values change. By studying a reaction at different concentrations, we often obtain heterometric curves, which if compared amongst themselves, supply additional information on the less soluble and on the more soluble compounds separately. Because of the different characteristics of both methods, occasionally a conductometric titration, which is adapted to a heterometric study, may be very helpful in giving further evidence on what happens in the solution, especially with regard to the partial reactions which occur. It must be born in mind that reactions in *solution* which lead to the formation of *soluble* undissociated compounds, are not observed in the heterometric curves. When the interpretation of a complicated heterometric curve is very difficult, a parallel conductometric titration may provide further evidence favouring a certain interpretation of the heterometric curve.

pH-Heterometry

Still more interesting is the combination of pH and heterometric titrations which mostly give far-reaching results. Both titrations can be carried out under identical conditions of concentration of the titrated solution and the titrant. By the addition of a suitable buffer mixture, a heterometric titration may be carried out at any pH thus giving the course of the chemical reaction in all its phases at the chosen pH. Parallel pH and heterometric titrations are essential to procuring detailed information about the pH-conditions for the formation and dissolution of a precipitate, the composition of which is known from previous heterometric titrations. For such titrations a suitable buffer mixture is chosen, a buffer which may not interfere in any way with the reaction as studied heterometrically. On gradual addition of a base the pH's range from 1 to 11, or by the dropwise addition of acid, the pH region from 11 to 1 may be investigated.

Such parallel pH-heterometric titrations give much valuable information and supply an abundance of facts which can be obtained by other methods only by lengthy and laborious procedures. The results of such titrations can be evaluated specially for, and find application in, macro or micro gravimetric and heterometric analysis. Another field in which such parallel pH-heterometric titrations are of immense importance is in the chemistry of complex formation and decomposition. From the heterometric pH curves, the pH conditions under which complexes exist may be established. The curves obtained are not limited to the study of one complex compound but frequently provide us with valuable information concerning the interrelation and the transformation of complexes into one another. It is very important for these parallel heterometric-pH titrations to chose a buffer mixture which does not itself form complexes with the cation of the reacting mixture. Generally the concentration of the active components will be between 0.1 %-1 % of the concentration of the buffer so that on dropwise addition of alkali or acid, the pH curve which is obtained is identical in the presence as well as in the absence of the reacting components. Once a suitable buffer mixture is chosen, we have only to draw one heterometric curve which compared with the blank pH curve provides the desired information. Fig. 2 presents a series of such heterometric pH curves as they were obtained from different reactions studied. Much space would be required to discuss the character of these curves in detail. A selection of such curves will be discussed by us in the special report dealing with the application of the heterometric method.

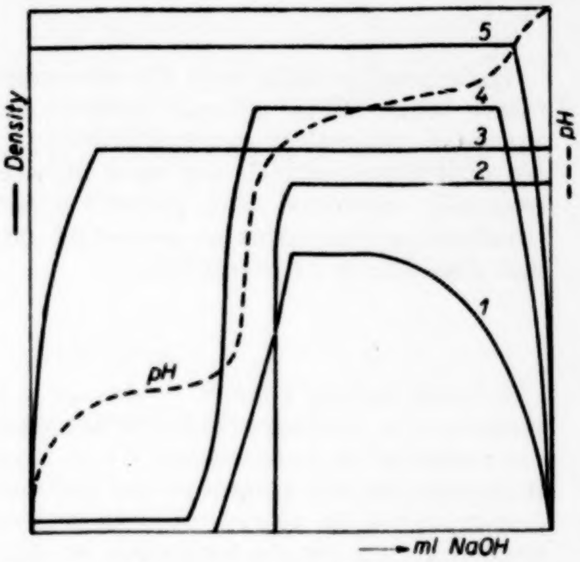

Fig. 2. pH-heterometric titration curves.

Adsorption and heterometry

A phenomenon which has to be considered when a solid phase appears is adsorption. Our extensive experience in heterometric titrations when analysing compounds containing micro or submicro quantities of cations, anions and neutral compounds is the following: when these were precipitated heterometrically from a concentrated solution of mono- bi- or polyvalent salts, *only in very few cases was there interference which could be explained by adsorption.* This is a fact of utmost importance in heterometry, because, if adsorption interfered with the measurements, the heterometric determination of minute quantities of an insoluble compound would be an illusion. It must be taken into consideration that so far all our heterometric titrations have been carried out at room temperature where the danger of adsorption is much greater than at higher temperatures. Of course, there can be no question that adsorption does occur, but it is important to know how far the adsorption interferes with the precise location of the critical points.

None of the problems encountered in gravimetry caused difficulties in the precipitation and the quantitative heterometric determination of end-points, using sodium and potassium hydroxides or salts of this and other metals. Barium could be determined heterometrically by titrating with disodium carbonate and calcium could be determined with trisodium phosphate with equal success. (On the other hand, we met with difficulties in the location of the end-point in the precipitation of lead chromate.)

We explain the lack of interference in so many cases, in the following way: in heterometry it is necessary to make a rigorous distinction between what are called the *solid* and the *liquid* phases, and *only the light absorption effect of the solid phase is measured.* The adsorbed layer, which consists of *solvated* ions, acts *as if it were still in the liquid phase,* and therefore has the same effect on the light transmittance as the liquid phase itself. In those cases where the light transmittance is affected by adsorption, we have to assume that partial or complete desolvation occurs, and the adsorbed ions act as if they were a part of the solid phase. It must be born in mind that most of the heterometric reactions studied by us were reactions between *ions* which are more or less solvated in the *polar* solvents used. It would be most interesting to extend the heterometric studies of adsorption to neutral molecules using non-polar solvents.

Another generally established fact which supports our view is the following: from our investigations we know that micro and submicro quantities of heterometrically analysed precipitates can be determined with precision from very strongly coloured salt solutions, provided that the coloured *ions* do not participate chemically in the reaction. The intensity of the colour does not change during the heterometric titration and the end-point can be located with precision. No coloured filters whatever are required, as the coloured solution by itself, acts as a filter of *constant* intensity. This very considerably simplifies the heterometric study of coloured solutions.

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SUMMARY

Heterometry deals with the photometric study of chemical reactions in suspensions on a quantitative basis. While a linear relation between the quantity of material and the light absorption is the basic condition in "turbidimetry", this situation is not generally observed in heterometry. No protective colloids are used in heterometry. The heterometric study of a chemical reaction is generally combined with parallel conductometric and pH-titrations. Parallel pH and heterometric titrations are essential for procuring detailed information about the pH-conditions for the formation and dissolution of precipitates.

RÉSUMÉ

L'hétérométrie permet le dosage quantitatif de composés chimiques en suspension. Contrairement à la turbidimétrie, il n'est pas nécessaire d'avoir une relation linéaire entre la quantité du composé et l'absorption de la lumière. L'adjonction de colloïde protecteur n'est donc pas indispensable en hétérométrie. L'étude hétérométrique d'une réaction chimique est généralement accompagnée de titrations conductométrique et pH-métrique permettant d'établir facilement les conditions de pH de formation et de dissolution des précipités.

ZUSAMMENFASSUNG

Die Heterometrie erlaubt eine quantitative Bestimmung von chemischen Verbindungen in Suspension. Im Gegensatz zu der Turbidimetrie ist es nicht notwendig, eine lineare Beziehung zwischen der Menge der Verbindung und der Lichtabsorption zu haben. Das Zugeben eines Schutzkolloïdes ist deshalb für die Heterometrie nicht nötig. Die heterometrische Untersuchung einer chemischen Reaktion ist gewöhnlich begleitet von konduktometrischen- und pH-metrischen Titrationen, welche gestatten, die pH-Bedingungen leicht festzusetzen, die notwendig sind für die Bildung und die Auflösung des Niederschlages.

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ESTIMATION OF SODIUM IN ALUMINIUM USING THE FLAME PHOTOMETER

by

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INTRODUCTION

Sodium is used to a considerable extent for grain refining of aluminium. This has lead to the necessity of estimating sodium as a routine operation. The accepted wet methods, such as precipitation as sodium uranyl acetate, take several hours to carry out and need the attention of a highly skilled analyst. It was thought that a flame photometric method would yield rapid results, sufficiently accurate for routine work.

DISCUSSION

It was assumed that only plain aluminiums would be analysed and that the interference due to other impurities would be ignored. This confined the work to the interference caused by aluminium on the sodium flame. The investigation was therefore carried out by taking four sets of solutions. In each set of solutions the aluminium concentration was kept constant, but the sodium concentration was varied. The intensity of the sodium flame was then measured for each solution.

Difficulty was found in making an aluminium solution sodium free, since even the small quantities present in pure reagents were detectable on the flame photometer and gave rise to too great an interference. This was finally overcome by precipitating the aluminium as $Al(OH)_3$ using NH_4OH, washing with distilled water until free from sodium and then redissolving in hot hydrochloric acid. The solution then gave a blank reading 0.2 p.p.m. which was considered satisfactory, bearing in mind that ordinary glass was used throughout which would give rise to some contamination.

RESULTS

As can be seen from Fig. 1, the presence of aluminium masks the sodium flame to a considerable extent. The greater the concentration of aluminium the greater the masking.

With increase in sodium concentration, at a constant aluminium concentration, we get the normal flame saturation effect causing a curved graph rather than a straight line relationship.

The routine method then would be to draw a calibration curve for sodium in the presence of a known concentration of aluminium. A known weight of sample is then taken and the solution controlled by dilution, or evaporation to contain the same concentration of aluminium as in the calibration curve. At all times a blank estimation must be run using the same reagents and quantities as in the analysis of the sample.

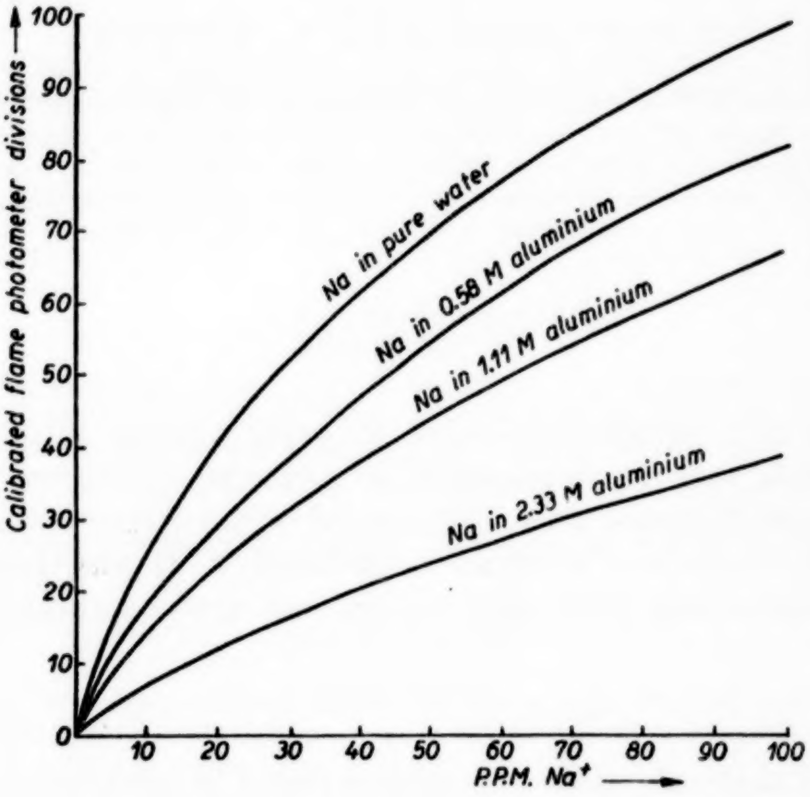

Fig. 1 Calibration curves for concentrations of aluminium shown.

EXPERIMENTAL

Reagents

Sodium solution. Dry AnalaR NaCl was weighed out and dissolved in sodium-free water to give 10,000 p.p.m. Na^+, *i.e.* 25.418 g NaCl/litre.

Aluminium solutions. Pure aluminium was dissolved in aqua regia. After dissolving, the aluminium was precipitated with NH_4OH filtered through No. 40 filter paper and washed free from sodium ions. The precipitation was then redissolved in the minimum of hot hydrochloric acid and made up to the required volume with sodium-free water. This solution contained about 0.2 p.p.m. of sodium.

Sodium-free water. Distilled water, passed down an anion and cation exchange resin mixture, was used in all cases.

Procedure

Three series of mixtures of sodium and aluminium were made up as given in the following tables. The intensity of the flame was then measured and the results plotted as shown in Fig. 1 which is a calibration curve for these concentrations of aluminium

TABLE I

In all cases the total volume was adjusted to 10 ml with sodium-free water. The sodium solution was measured with an Agla syringe.

Sample	*Conc. of sodium required in p.p.m.*	*ml of sodium solution taken*	*ml of Aluminium*	*Deflections (average of 4 readings)*
Series I.				
1	3	0.003	Nil	9.4
2	5	0.005	,,	15.6
3	10	0.010	,,	25.0
4	15	0.015	,,	34.0
5	20	0.020	,,	41.2
6	25	0.025	,,	47.5
7	50	0.050	,,	70.4
8	100	0.100	,,	100
Series II. Al soln. 0.58*M*.				
1	5	0.005	9.9 ml	14.0
2	20	0.020	,,	28.8
3	25	0.025	,,	35.0
4	50	0.050	,,	55.0
5	100	0.100	,,	81.5
Series III. Al soln. 1.1*M*				
1	5	0.005	9.9 ml	7.1
2	10	0.010	,,	14.1
3	15	0.015	,,	18.1
4	25	0.025	,,	28.2
5	50	0.050	,,	44.9
6	75	0.075	,,	56.7
7	100	0.100	,,	67.4
Series IV Al soln. 2.33*M*				
1	10	0.010	9.9 ml	6.6
2	20	0.020	,,	11.1
3	30	0.030	,,	16.0
4	50	0.050	,,	24.1
5	75	0.075	,,	32.0
6	100	0.100	,,	39.8

All series were standardized to 0 and 100 p.p.m. with water and sodium solution in the normal way.

Results obtained on solutions containing less than 5 p.p.m. of sodium were erratic and not recorded.

Recommended routine procedure

For routine analysis, the following procedure was found to be successful.

Prepare calibration curves for the conversion of sodium flame intensity to sodium concentration in the presence of constant amounts of aluminium, as described in the experimental section.

Take 0.25 g of aluminium, dissolve in 10 ml of conc. hydrochloric acid. Transfer to a 100 ml standard measuring flask and make up to the mark with sodium-free water. Measure the sodium flame intensity on the flame photometer and read off the sodium concentration from the calibration curve made out for this concentration of aluminium.

A blank determination must be run by putting on at the same time 10 ml of conc. hydrochloric acid in a similar beaker. This is transferred to a standard measuring flask at the same time as the sample and made up to the mark. The sodium concentration is read off the aluminium-free calibration curve and the result subtracted from the result found on the sample in the normal way.

Conclusions

The results obtained show that the flame photometer can be used for a rapid routine method of estimating sodium in pure aluminium. There appears to be no reason why the same principle cannot be applied to the analysis of aluminium alloys. Further work will be carried out in this direction.

ACKNOWLEDGEMENTS

The authors wish to thank Brigadier HARRIS, Eng. in Chief, G.P.O. for permission to publish this work and to Mr. J. TOWNLEY who carried out much of the experimental work.

SUMMARY

A flame photometric method of estimating sodium in aluminium has been developed. It was found that the concentration of aluminium altered the intensity of the sodium flame. This necessitated using standard conditions.

RÉSUMÉ

Une méthode est proposée pour le dosage du sodium dans l'aluminium par photométrie de flamme. On a constaté que la teneur en aluminium fait varier l'intensité de la flamme de sodium; ce qui nécessite l'établissement de conditions standard.

ZUSAMMENFASSUNG

Es wird eine Methode vorgeschlagen, um Natrium in Aluminium zu bestimmen, mit Hilfe der Flammenphotometrie. Man hat festgestellt, dass der Gehalt an Aluminium die Intensität der Natriumflamme variiert; was eine Standardisierung der Bedingungen benötigt.

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COULOMETRIC TITRATION OF THALLOUS ION WITH ELECTROGENERATED FERRICYANIDE ION

by

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In a previous paper[1] we demonstrated the successful application of electrogenerated ferrocyanide ion for the coulometric titration of zinc. In the present study the coulometric application of the ferro-ferricyanide couple has been extended to redox titrations, and specifically to the titration of thallous ion according to

$$\mathrm{Tl^{+} + 2Feic + 3\ OH^{-} = Tl(OH)_3 + 2Feoc}$$

The titration of thallous ion with standard ferricyanide solution in the ordinary way was originally studied by DEL FRESNO AND VALDES[5]. In the method described herein the requisite ferricyanide ion is generated electrolytically by the oxidation of ferrocyanide ion at a platinum anode in a strongly alkaline solution containing a relatively large concentration of ferrocyanide ion. The equivalence point is detected either potentiometrically or amperometrically.

In acid medium the thallous-thallic couple is strongly oxidizing[2],

$$\mathrm{Tl^{+3} + 2e = Tl^{+}};\ E^\circ = +1.25\ \mathrm{V.}\ vs.\ \mathrm{N.H.E.}$$

However, the great insolubility of thallic oxide and the solubility of thallous hydroxide renders the couple strongly reducing in alkaline medium,[2]

$$\mathrm{Tl(OH)_3 + 2e = Tl^{+} + 3\ OH^{-}};\ E^\circ = -0.05\ \mathrm{V.}\ vs.\ \mathrm{N.H.E.}$$

The ferri-ferrocyanide couple is also somewhat dependent on acidity as shown by the formal potentials[3]

$$\mathrm{[Fe(CN)_6]^{-3} + 2H^{+} + e = H_2Fe(CN)_6^{-2}};\ E' = +0.71\ \mathrm{V.}\ (1M\ \mathrm{HCl})$$
$$\mathrm{[Fe(CN)_6]^{-3} + e = [Fe(CN)_6]^{-4}};\ E' = +0.48\ \mathrm{V.}\ (1M\ \mathrm{NaOH})$$

From these data it is evident that the titration of thallous ion with ferricyanide ion is feasible only in strongly alkaline medium.

APPARATUS AND REAGENTS

The coulometric titration cell was essentially that previously described.[1] The constant current supply[6] maintained the current constant to ± 0.01%. The progress of the titration was followed by observing the potential of a platinum indicator electrode against a saturated calomel reference electrode with a potentiometer in the ordinary manner.

Because ferrocyanide ion undergoes slow decomposition in alkaline medium, the supporting electrolyte was prepared freshly for each titration and was protected from strong light. Solutions prepared by adding weighed amounts of solid sodium hydroxide and potassium ferrocyanide to dearated water in the light-protected electrolysis cell resulted in a reagent blank of 1.5 ± 0.5 seconds generation time at 60 milliamperes current (*i.e.*, 0.09 coulomb), when the concentrations of sodium hydroxide and potassium ferrocyanide were 2 and 0.05M, respectively. This blank was so constant that for most titrations 0.09 coulomb was generated and the resulting equilibrium potential was taken as the potential to which the titration was carried.

Thallous chloride solutions were prepared determinately from the recrystallized salt dried at 120° C. The titer of the stock solution was verified by coulometric titration using the method of BUCK, FARRINGTON, AND SWIFT[7] modified to the extent of using potentiometric, rather than amperometric, end-point detection. Results agreed with the determinate value to within 0.05%.

RESULTS AND DISCUSSION

Effect of hydroxide concentration. From the net titration reaction one would expect more complete reaction, and hence greater magnitude of potential change at the e.p., the greater the concentration of hydroxide ion. This has been verified. However, the rate of establishment of potential equilibrium becomes inconveniently slow at very high concentrations of sodium hydroxide. Experiments were carried out at varying concentrations of sodium hydroxide to determine the optimum concentration compatible with accuracy and speed of titration. A typical series is shown in Fig. 1. With only 0.5M sodium hydroxide the rate of potential change is too small for satisfactory precision. With 4M sodium hydroxide the time required to establish potential equilibrium is inconveniently long. A concentration of 2M is about optimum.

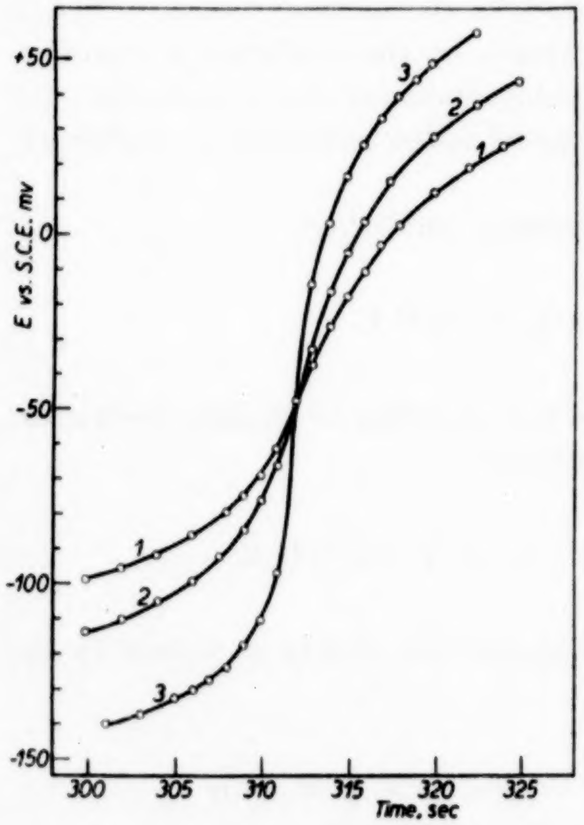

Fig. 1. Influence of sodium hydroxide concentration. Twenty mg of thallous ion in 125 ml of 0.18M potassium ferrocyanide in presence of (1) 1, (2) 2, and (3) 4M sodium hydroxide.

Effect of ferrocyanide concentration. The effect of ferrocyanide concentration on the titration curve is shown in Fig. 2. As expected the magnitude of the potential change at the e.p. is greater the smaller the ferrocyanide concentration.

In coulometric titrations one deals with a titration curve less favorable than that for the same titration done in the ordinary manner because the titration is carried out in the presence of a relatively very large excess of one of the products of the reaction (*e.g.*, ferrocyanide ion), which decreases the rate of change of potential at the e.p. For this reason titrations are best carried out with the minimum concentration of ferrocyanide sufficient to stabilize the working anode at a potential well below that for oxidation of water so that the generation of ferricyanide ion will proceed with 100% current efficiency. This concentration is dependent on cell geometry, rate of stirring, electrode design and area, and, of course, on the electrochemical characteristics of the particular generating reaction, and must be determined experimentally with the electrolysis cell to be used.

In the present case the oxidation of ferrocyanide to ferricyanide ion proceeds with 100% current efficiency in 0.05*M* ferrocyanide solution at a current density up to 8 mA/cm², corresponding to a maximal current of about 60 milliamp with the particular platinum anode used.

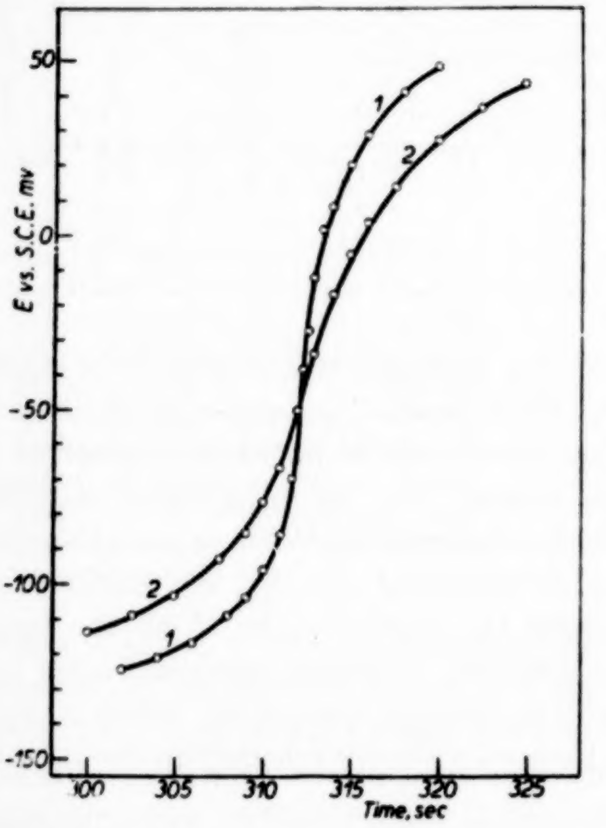

Fig. 2. Effect of ferrocyanide ion concentration in titration of 20 mg of thallous ion in 125 ml of 2*M* sodium hydroxide. (1) 0.04 and (2) 0.18*M* potassium ferrocyanide.

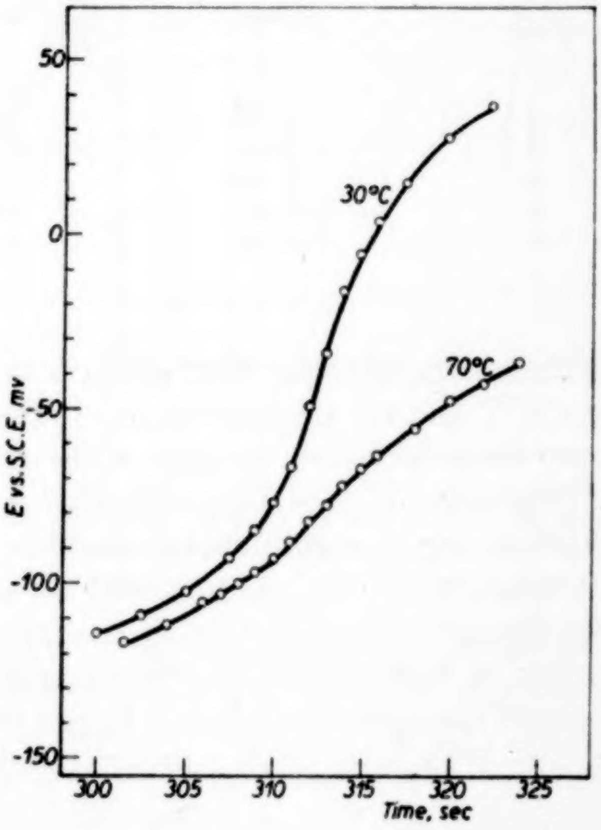

Fig. 3. Influence of temperature in titration of 20 mg of thallous ion in 0.18*M* potassium ferrocyanide and 2*M* sodium hydroxide.

Influence of temperature. The reaction between thallous ion and ferricyanide ion is quite slow at room temperature. At an elevated temperature equilibrium is established more rapidly, but, as shown in Fig. 3, the magnitude of the potential change at the e.p. is greatly decreased. Consequently all subsequent titrations were performed at room temperature.

Effect of light and oxygen. Preliminary experiments with the method had shown moderately large negative errors corresponding to an apparent current efficiency of over 100%. These were traced to the presence of dissolved oxygen, and to light decomposition of the ferrocyanide. When solutions were made immediately before use by dissolving the appropriate amount of solid sodium hydroxide in water, covering the cell with light tight paper before adding the solid potassium ferrocyanide, and immediately deaerating the solution with nitrogen the blank became small and constant and results were precise to 0.1%.

Performance data. Table I summarizes the results of twenty-two trial titrations of 4 to 40 mg of thallous ion in a volume of 125 ml. The amounts of "thallium found" are the averages for the indicated number of trials.

TABLE I

TITRATION OF THALLOUS ION WITH ELECTROGENERATED FERRICYANIDE ION

Volume of solution was 125 ml and it contained $2M$ sodium hydroxide and $0.05M$ potassium ferrocyanide. Generating currents from 16 to 62 milliamp were used and titration times ranged from 123 to 615 sec.

No. of Trials	*Thallium, mg.* *Taken*	*Found Av.*	*Av. Error %*	*Av. Deviation %*
5	4.088	4.112	+0.6	+1.0
3	8.148	8.148	0.0	±0.14
5	8.169	8.159	—0.12	±0.16
4	16.30	16.30	0.0	±0.18
6	40.80	40.51	—0.75	±0.5

In the optimum range from about 8 to 20 mg, the average error is seen to be smaller than 0.2%, and the precision is about the same. With smaller quantities of thallous ion the precision decreases because of the relatively small rate of potential change at the e.p. However, by employing a smaller solution volume (*e.g.*, 25 ml) smaller quantities of thallium (*e.g.*, 1 mg) doubtless could be titrated satisfactorily. With 40 mg of thallium the average error was —0.75% with an average deviation of ±0.5%. We attribute this to significant coprecipitation of thallous ion with the thallic oxide. With the largest quantity of thallous ion the time required to establish a steady potential after each increment of generation was also longer than with the smaller quantities, which is understandable if thallous ion is coprecipitated and then only slowly released to the solution.

Amperometric end-point detection. The possibility of detecting the end-point of the titration amperometrically was also investigated. The amperometric system consisted of a platinum electrode in the test solution in conjunction with a saturated calomel auxiliary electrode, the platinum electrode being polarized cathodically. With a constant applied voltage such that the potential of the platinum is greater than the reduction potential of ferricyanide ion but smaller than the reduction potential of thallous ion, the observed indicator current remains virtually zero up to the e.p., and then increases linearly due to reduction of the excess ferricyanide ion beyond the e.p. An ordinary polarograph served as the measuring apparatus.

To establish the optimum applied voltage (polarization potential against the saturated calomel electrode), current-voltage curves of small concentrations of thallous ion, and of solutions containing ferro- and ferricyanide ions, were separately determined with a platinum microelectrode in the usual manner. Typical curves in air-free, $2M$ sodium hydroxide are shown in Fig. 4. The currents have been corrected for the small background current obtained with the supporting electrolyte alone. These curves demonstrate that an applied potential between —0.15 and —0.30 V is optimum to produce an indicator current which will remain very small and constant before the e.p. and which will increase sharply at the e.p.

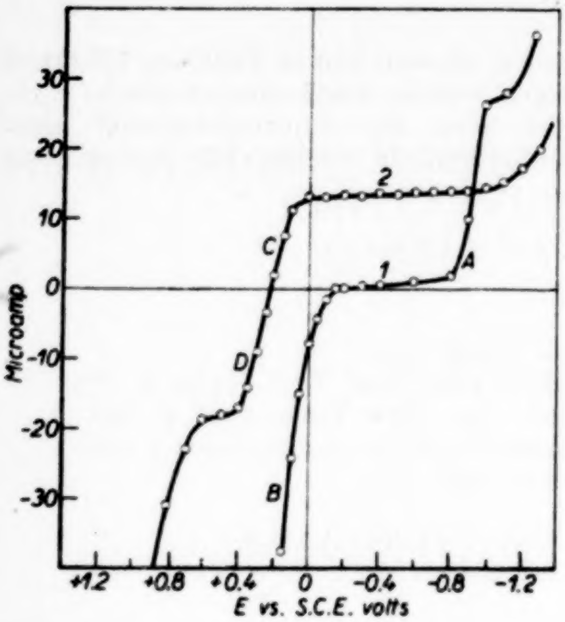

Fig. 4. Polarization curves with platinum microelectrode of (1) 1 mM thallous ion and (2) a mixture of 0.5 mM each of ferro- and ferricyanide ions, in 2M sodium hydroxide. *A* corresponds to reduction of thallous ion to metal, *B* to oxidation of thallous ion to thallic oxide, *C* to reduction of ferricyanide ion, and *D* to oxidation of ferrocyanide ion.

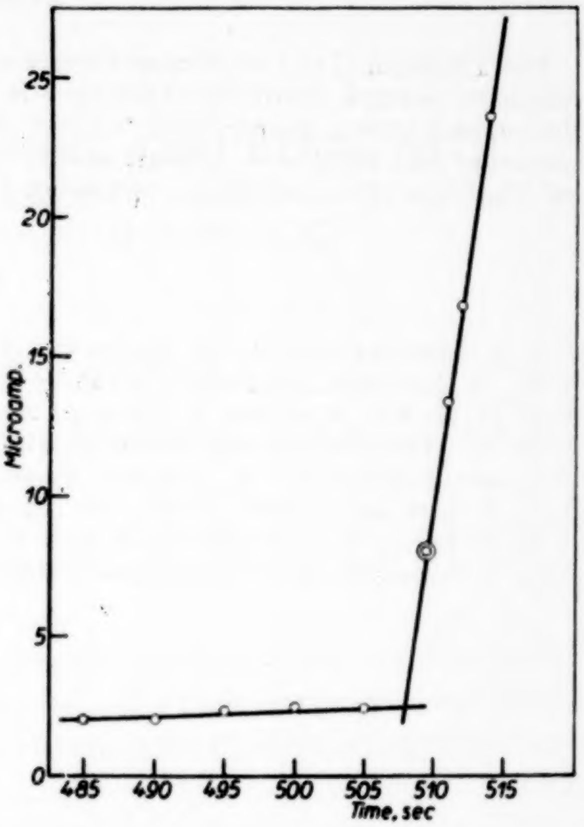

Fig. 5. Amperometric titration curve of 16 mg of thallous ion in 125 ml of 2M sodium hydroxide and 0.05M potassium ferrocyanide with potential of platinum indicator electrode at -0.15 V/*vs.* S.C.E.

Curve 5 shows a typical amperometric titration curve. The e.p. is practically at the extrapolated intersection of the two linear parts of the graph. However, because the ferrocyanide supporting electrolyte must be pre-titrated to correct for the effect of impurities, the most expeditious procedure in practice is as follows. The supporting electrolyte alone is first placed in the cell and generation is carried out until a small excess of ferricyanide ion is present, and the indicator current is noted. The sample of deaerated thallous solution is then added, and generation is performed until the indicator current is restored to the same value as in the pre-titration. In this way 16 mg samples of thallous ion could be titrated with a precision and accuracy of ±0.1%.

ACKNOWLEDGEMENT

We gratefully acknowledge partial financial support of this study by the Mallinckrodt Chemical Works.

Appreciation is also expressed to Merck and Co. for sponsoring the Merck Fellowship in Analytical Chemistry whose benefits were enjoyed by one of us (A.M.H.) during 1954-55.

SUMMARY

Thallous ion can be coulometrically titrated to thallic oxide in strongly alkaline medium by means of ferricyanide ion generated by anodic oxidation of ferrocyanide ion at a platinum anode. The equivalence point may be detected either potentiometrically or amperometrically. With 8 to 20 mg of thallous ion in 125 ml the accuracy and precision are within ± 0.2%.

RÉSUMÉ

Les ions thallium(I) peuvent être titrés par oxydation coulométrique en oxyde de thallium(III) en solution fortement alcaline au moyen d'un ferricyanure, formé par oxydation anodique d'un ferrocyanure à l'anode de platine. Le point d'équivalence peut être déterminé soit par potentiométrie, soit par ampérométrie. Pour 8 à 20 mg/125 ml d'ion thallium(I) la précision est de l'ordre de ± 0.2%.

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ZUSAMMENFASSUNG

Die Thallium (I)-Ionen können titriert werden, indem man sie coulometrisch zu Thallium III-Oxyd oxydiert, in stark alkalischer Lösung, mit Hilfe von Ferricyanid, welches durch eine anodische Oxydation von einem Ferrocyanid, an der Platinanode gebildet wird. Der Äquivalenzpunkt kann entweder mit Hilfe von Potentiometrie oder Amperometrie festgestellt werden. Für 8-20 mg/125 ml Thallium (I)-Ionen ist die Präzision ungefähr ± 0.2%.

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HIGH FREQUENCY TITRATIONS INVOLVING CHELATION WITH ETHYLENEDIAMINETETRAACETIC ACID

IV. COMPLEXATION OF THORIUM NITRATE

by

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The primary purpose of the investigation of the chelation of thorium ion was to establish the feasibility of following the reaction by means of a high frequency oscillator. The ultimate aim was to provide an oscillometric titration for thorium using ethylenediaminetetraacetic acid as the titrant. A number of related studies have been reported by other investigators. BRINTZINGER and his associates prepared[1] a complex having a composition of $Th(C_{10}H_{12}N_2O_8) \cdot 2\,H_2O$. CAMBELL established the formation of definite and stable salts of thorium ethylenediaminetetraacetate using potentiometric methods[2]. Quantitative procedures for determining thorium with ethylenediaminetetraacetic acid have been proposed. FRITZ AND FORD[3] have described a method utilizing a color indicator for disclosing the end-point of the titration, and MALMSTADT AND GOHRBANDT have proposed a method which utilizes a spectrophotometric procedure for establishing stoichiometry[4]. The use of high frequency titrations for the determination of thorium has been suggested by BLAEDEL AND MALMSTADT[5] who used oxalate on the titrant.

The high frequency oscillator has proved to be a versatile tool for studying chelation reactions and following compleximetric titrations[6]. In the present case complexation should result in the release of four protons from the complexing organic acid,

$$H_4Y + Th^{+4} \rightarrow 4\,H^+ + ThY$$

(H_4Y symbolizes ethylenediaminetetraacetic acid) and their release should be capable of being followed by high frequency titration using standard base as the titrant. The direct oscillometric titration using standard solutions of ethylenediaminetetraacetic acid or its salts should also be possible.

EXPERIMENTAL

Reagents and solutions

Standard solutions of ethylenediaminetetraacetic acid and its salts were prepared from reagent grade chemicals. Standardizations were made against calcium or copper salts. Solutions to be used for quantitative determinations of thorium were checked against pure thorium salts. Stock solutions of thorium (1/10M) were prepared from reagent grade $Th(NO_3)_4 \cdot 4\,H_2O$ and standardized by precipitation of the oxalate with subsequent ignition and weighing as ThO_2.

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Apparatus

A Sargent Model V Oscillometer was used to follow the course of all titrations. All reactions were carried out directly in the large titration cell (100 ml) without use of the cell compensation unit. A Beckman Model G pH meter was used for determining hydrogen ion concentrations.

Reacting ratios of thorium ion and ethylenediaminetetraacetic acid

The determination of reacting ratios was approached in two ways. In one method, hydrogen ions released through chelation were titrated with standard base; and in the other approach, known amounts of ethylenediaminetetraacetic acid were titrated directly with standard thorium solution.

I. *Liberation of hydrogen ion.* One hundred ml of 1/3032*M* ethylenediaminetetraacetic acid were placed in the titration cell of the Oscillometer. Known amounts of standard thorium nitrate were then added and the hydrogen ions released by the ensuing reaction were titrated with 1/90.0*M* sodium hydroxide. Various ratios of metal ion to complexing addendum were titrated so as to make certain that the true reacting ratio was approached and surpassed. The results of these studies are graphically presented in Fig. 1. When

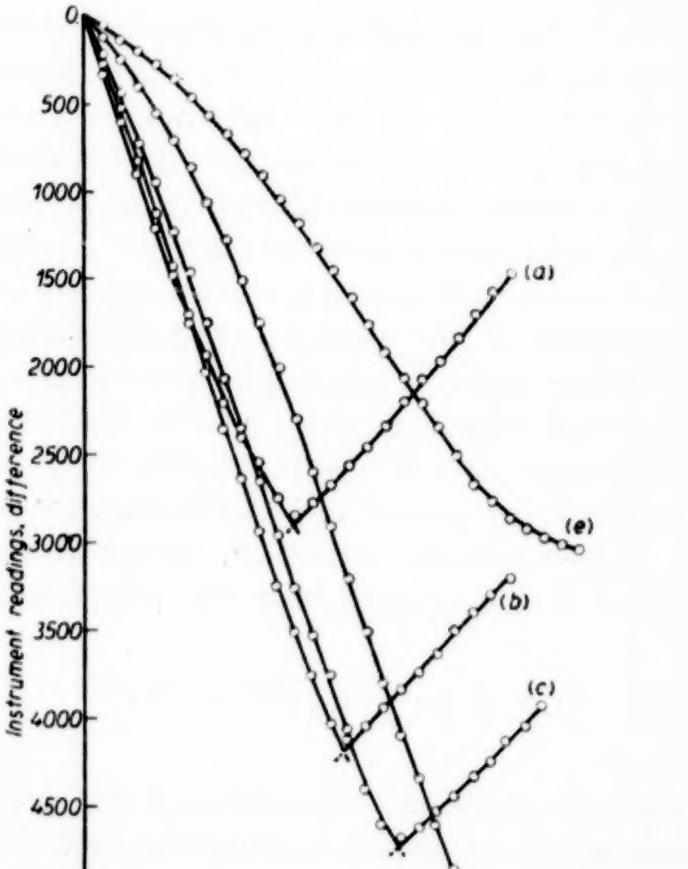

Fig. 1. Sodium hydroxide titration of thorium nitrate and EDTA.
(a) Addendum only
(b) 1:4 (Th: addendum)
(c) 1:2 (Th: addendum)
(d) 1:1 (Th: addendum)
(e) 2:1 (Th: addendum)

no thorium is present, simple titration of the addendum yields a curve having an inflection point at 2 mole equivalents of base. As the ratio of thorium to ethylenediaminetetraacetic acid is increased, the inflection point is displaced increasingly to the right until a 1 to 1 ratio is obtained. At this point, all of the salinogenic hydrogens of the addendum have been released, indicating that the ultimate ratio of mole to mole reactants is attained. Thorium in excess of the 1 to 1 ratio cannot release additional hydrogen ions but does consume additional base, probably through direct reaction. Ratios of thorium to addendum greater than 1 to 1 do not yield titration curves showing reversal points.

II. *Determination of reacting ratios through direct titration.* The thorium complex of ethylenediaminetetraacetic acid is very stable and for this reason lends itself to study by direct Oscillometric titration. The complexing acid itself shows little influence on the response of the high frequency titrimeter. Upon titration with thorium ion there is an immediate formation of the stable complex with consequent liberation of hydrogen ions. The instrument is very sensitive to the change in hydrogen ion concentration and increased readings are obtained until the stoichiometric end-point is attained (1 to 1). Addition of thorium ion beyond the end-point causes some further increase in instrument readings but the rate of increase is much less and a sharp inflection in the titration curve gives clear indication of the point of equivalence (Fig. 2).

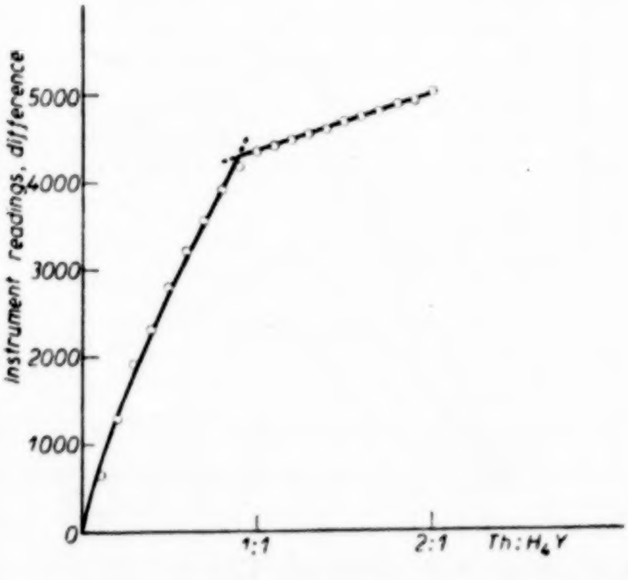

Fig. 2. Titration of 1/3000*M* EDTA with 1/150*M* thorium nitrate.

Quantitative determination of thorium

The quantitative determination of thorium can be accomplished by either the alkalimetric titration of liberated hydrogen ions or by direct titration of thorium ion with di-sodium ethylenediaminetetraacetate. In the first method, a solution of thorium is added to an excess of ethylenediaminetetraacetic acid and the released hydrogen ions are titrated with standard base. Chelation causes the liberation of protons equivalent to the amount of added thorium and thus is the basis for a method of quantitatively estimating thorium. Because the method is not as convenient as the direct titration procedure and because the technique employed has been described in a general way under the discussion of reacting ratios, detailed description of procedure will not be given.

Direct oscillometric titration of thorium by means of di-sodium ethylenediaminetetraacetate provides an excellent means of determining thorium. Very dilute solutions of the sample can be titrated with relative accuracy, permitting semimicro and micro-analysis of thorium in macro volumes of sample. This is illustrated by the following procedure which was used in establishing the feasibility of the direct titration approach.

One hundred ml of test solution were placed in the large titration cell of the Oscillometer and titrated directly with standard di-sodium ethylenediaminetetraacetate. The solution was stirred with a motor driven stirrer having a glass impeller. The titrations were conducted in unbuffered solutions. Typical concentrations used and characteristic curves are shown in Fig. 3. The concentration of the thorium solution is of primary importance and concentrations of 1/1000 to 1/5000*M* were found to be optimum. In all titrations, curves were obtained which ascended steeply with addition of titrant, breaking sharply at the end-point. The reproducibility and accuracy that can be expected are indicated in Table 1.

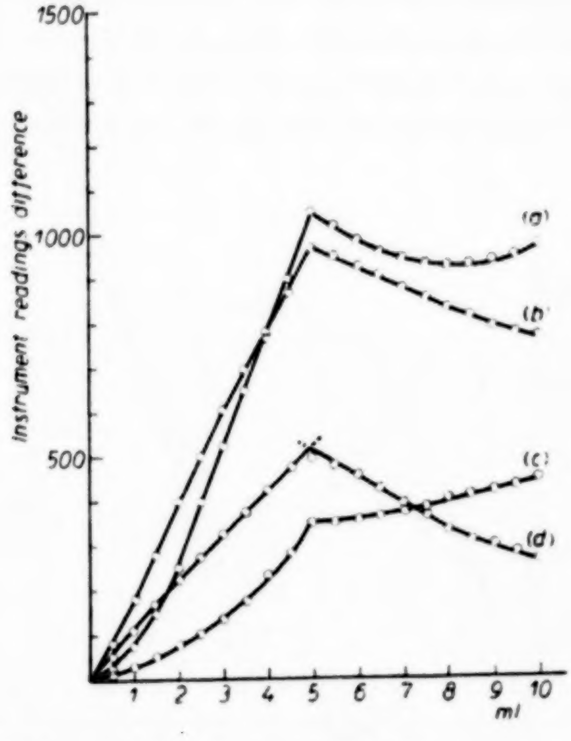

Fig. 3. Titrations of thorium nitrate with disodium EDTA
(a) 1/3015*M* thorium nitrate with 1/150*M* disodium EDTA
(b) 1/1000*M* thorium nitrate with 1/50.1*M* disodium EDTA
(c) 1/6023*M* thorium nitrate with 1/300*M* disodium EDTA
(d) 1/504*M* thorium nitrate with 1/25.2*M* disodium EDTA

TABLE I

TYPICAL ANALYTICAL RESULTS

Th present (mg)	*Molarity of titrant*	*Th found (mg)*	*Per cent error*
7.699	1/150	7.737	0.49
7.699	1/150	7.737	0.49
9.239	1/203	9.285	0.50
9.239	1/203	9.285	0.50

Interferences

All electrolytes tend to "load" the Oscillometer and so reduce its sensitivity. Consequently, every effort should be directed toward keeping electrolyte concentrations as low as possible. Apart from loading effects, chloride, bromide, iodide, bromate, chlorate, thiocyanate, iodate and sulfate were without deleterious effects on the titration of thorium. Acetates, oxalates and fluorides masked the titration and were the only anions found to give serious interference. The masking effects results from the formation of the respective thorium complexes which have sufficient stabilities that they may form in competition with the ehylenediaminetetraacetate complex.

Because ethylenediaminetetraacetic acid is a very general complexing agent, most heavy metals interfere with the thorium determination. Some flexibility can be derived, however, due to the differences that exist in the relative stabilities of the complexes of the various metals. In the case of metals such as barium, strontium, silver, thallium(I), and the alkali metals, no interferences are encountered other than the usual loading effects. Barium and strontium nitrates gave heavier loading effects than other salts studied.

TABLE II

TITRATIONS IN THE PRESENCE OF DIVERSE SALTS

Th present (mg)	*Salts added (mg)*	*Th found (mg)*	*Per cent error*
7.734	5.66 ($AgNO_3$)	7.802	0.88
7.734	13.07 ($Ba(NO_3)_2$)	7.830	1.25
7.734	7.40 (KCl)	7.53	0.25

DISCUSSION

High frequency titrations serve to confirm the formation of the 1 to 1 complex of thorium ethylenediaminetetraacetate as reported by other workers using different experimental approaches. When a mixture of ethylenediaminetetraacetic acid and thorium is titrated with sodium hydroxide, only one inflection point is obtained on the titration curve, the shape of the curve being similar to that obtained with cobalt, nickel, copper, zinc, cadmium, and manganese[6]. The nature of the curve indicates that thorium is chelated with the acid addendum with accompanying release of hydrogen ions. The titration curves are therefore simply those of the acid-base titrations as resulting from the liberated protons.

Because free ethylenediaminetetraacetic acid exhibits a pH of 2.8 to 3.0, complex formation with thorium must take place under acidic conditions. In fact, when sodium salts of ethylenediaminetetraacetic acid were titrated with thorium at high pH values ($\sim$10) a complicated curve was obtained that was not readily interpreted. The general indication was that the chelates formed in high pH ranges are not sufficiently stable to permit their direct formation by stoichiometric reaction. FRITZ AND FORD[3] suggested that a pH range of 2.3 to 3.4 should be used in the titration of thorium with ethylenediaminetetraacetic acid and the present investigation confirms this.

In the direct titration with di-sodium ethylenediaminetetraacetate, the release of two protons occurs during the reaction and there is a consequent decrease in pH. Because the solutions titrated were so dilute, however, the changes encountered in the present studies were not enough to cause difficulty. For example, in the titration of 1/3000*M* thorium nitrate, the solution showed a pH of 3.4 at the start and was still within the lower pH limit at the end-point. The use of hydrochloric acid-potassium chloride buffer, did not improve the end-point as compared with titrations in unbuffered solutions. Titrations at higher pH with tri-or tetra-sodium ethylenediaminetetraacetates failed to give reproducible results.

ACKNOWLEDGEMENT

The authors wish to express their appreciation to E. H. Sargent and Company for financial support of this study. Ethylenediaminetetraacetic acid and its salts were kindly supplied by the Berswerth Chemical Company.

SUMMARY

High frequency titrations have confirmed the reacting ratio of thorium to ethylenediaminetetraacetic acid to be 1 to 1. It has also been shown that thorium can be determined by oscillometric titration using either the hydrogen release method or the direct titration technique. The method is especially interesting for the determination of small amounts of thorium in dilute solution.

RÉSUMÉ

Des titrations à haute fréquence ont confirmé le rapport 1 : 1, obtenu entre le thorium et l'acide éthylène-diaminotétraacétique. Il a été également démontré que le thorium peut être dosé par titration oscillométrique, soit par la méthode de libération des ions hydrogène, soit par la méthode de titration directe. La méthode est spécialement avantageuse pour le dosage de faibles teneurs de thorium en solution diluée.

ZUSAMMENFASSUNG

Die Hochfrequenztitrationen haben das Verhältnis 1 : 1 bestätigt für die Verbindung zwischen dem Thorium und der Äthylendiaminotetraessigsäure. Es wurde ebenfalls gezeigt, dass das Thorium auch mit einer oszillometrischen Titration bestimmt werden kann, sei es durch Freilegen der H-Ionen, sei es durch direkte Titration. Die Methode ist besonders vorteilhaft für schwache Gehalte an Thorium in verdünnten Lösungen.

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STUDIES ON NESSLER'S REAGENT
PART I

by

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The reagent made of HgI_2 (1 mol) and KI (2 mol) and rendered strongly alkaline with caustic alkalis, was first introduced by NESSLER[1] for the qualitative detection of ammonia as well as its quantitative estimation. Since then it has been used as the most sensitive test for ammonia and is well known as Nessler's reagent. Nothing is known regarding what happens when the components are mixed in aqueous solution. PÉLABON[2], however, has studied the action of KOH solutions of various strengths on HgI_2 and isolated only the solid products which separated. When HgI_2 is dissolved in KI solution, mercury is proved to exist as $[HgI_4]^{-2}$ ions by various physico-chemical methods[3]. The pK value of the dissociation, $[HgI_4]^{-2} \rightleftharpoons Hg^{+2} + 4I^-$ is 30.3. In the above solution there is no evidence of the existence of $[HgI_3]^-$ ion, although the phase-rule study[4] of the ternary system KI-HgI_2-H_2O leads to the stable solid phase of the composition $K[HgI_3.H_2O]$. The solution of one mole of HgI_2 in two moles of KI may therefore be regarded as containing one mole of $[HgI_4]^{-2}$ ion.

When a solution of $[HgI_4]^{-2}$ is allowed to react with ammonium hydroxide in absence of caustic alkali, there is no such characteristic brown colour but a white precipitate of $HgI_2.2NH_3$[5]. The presence of caustic alkali is therefore indispensable for Nessler's test; probably its chief role is to form an intermediate compound with $[HgI_4]^{-2}$, which gives the characteristic test with ammonia.

In order to discover the nature and composition of the intermediate product, an attempt has been made here to arrive at it by the following physico-chemical method, assuming that the reaction between $[HgI_4]^{-2}$ and OH^- ions may take place in one of the following ways.

$$[HgI_4]^{-2} + mOH^- \rightleftharpoons \left[Hg \begin{matrix} (OH)_m \\ I_{(4-n)} \end{matrix} \right]^{-(m-n+2)} + nI^- \quad \ldots\ldots\ldots\ldots\ldots (1)$$

$$2[HgI_4]^{-2} + mOH^- \rightleftharpoons \left[Hg_2 \begin{matrix} (OH)_m \\ I_{(8-n)} \end{matrix} \right]^{-(m-n+4)} + nI^- \quad \ldots\ldots\ldots\ldots\ldots (2)$$

As the alkali is present in large excess, the apparent equilibrium constant K' for (1) or (2) is given by

$$K' = \frac{\left[\frac{I}{n}\right]\left[I\right]^{n}}{\left[A - \frac{I}{n}\right]} \text{ ; } i.e., \text{p}\left(A - \frac{I}{n}\right) = (n + 1)\,\text{pI} + \log nK' \quad \dots\dots\dots\dots\dots \quad (3)$$

$$\text{or } K' = \frac{\left[\frac{I}{n}\right]\left[I\right]^{n}}{\left[A - \frac{2I}{n}\right]^{2}} \text{ ; } i.e., \text{p}\left(A - \frac{2I}{n}\right) = \frac{(n+1)}{2}\,\text{pI} + \log\sqrt{nK'} \quad \dots\dots\dots\dots \quad (4)$$

respectively, where $[A]$ = the initial concentration of $[HgI_4]^{-2}$ and $[I]$ = the concentration of iodide ion.

From the following concentration cells of iodide-hypoiodite system, the values of $[I]$ have been determined from the observed e.m.f.'s according to the relation, $E = 0.03 \log \frac{I_o}{I}$ at 30° C as KOH and IO^- present in both the cells are of the same concentration

$$\text{Pt} \left| \begin{array}{c} KOH + IO^- \\ + I^- \ (I) \end{array} \right| \begin{array}{c} \text{Saturated} \\ KCl \end{array} \left| \begin{array}{c} KOH + IO^- \\ + I^- \ (I_o) \end{array} \right| \text{Pt}$$

Now if (I_o), the concentration of iodide ion in one cell is known, then pI may be calculated as being equal to $\left(\frac{E}{.03} + \text{pI}_o\right)$. The values of pI thus obtained, have been plotted against the corresponding values of $\text{p}\left(A - \frac{I}{n}\right)$ or $\text{p}\left(A - \frac{2I}{n}\right)$ assuming n to be equal to 1, 2 or 3 in (1) or 1, 2, 3, 4, 5, 6 or 7 in (2); straight lines have been drawn through the average points and the slopes in each case have been determined and compared with the corresponding theoretical values. From the values thus obtained, it has been found only in the case when $n = 2$ in (1), that both the extrapolated and the theoretical values are equal. The reaction between $[HgI_4]^{-2}$ and OH^- ions may thus be assumed as

$$[HgI_4]^{-2} + m\,OH^- \rightleftarrows \left[Hg\begin{matrix}(OH)m \\ I_2\end{matrix}\right]^{-m} + 2I^-$$

and the apparent equilibrium constant $K' = \frac{[I]^3}{2\left[A - \frac{I}{2}\right]}$ and the equilibrium constant $K = \frac{[I]^3}{(B)^m.\ 2\left[A - \frac{I}{2}\right]} = \frac{K'}{[B]^m}$, where $[B]$ = the concentration of KOH.

Now the value of m can easily be calculated from the following relations

$$\frac{K'_1}{[B_1]^m} = \frac{K'_2}{[B_2]^m} = \frac{K'_3}{[B_3]^m}$$

$$\text{or } m = \frac{\text{Difference of p}K'\text{ values}}{\text{Difference of corresponding pB values}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

and it has been found to be approximately equal to 2 (see EXPERIMENTAL). Thus the nature of the reaction between $[HgI_4]^{-2}$ and OH^- ions has been established and the equilibrium constant K has also been calculated and found to be $10^{-3.26}$.

The composition of the coloured precipitate formed on addition of ammonia to Nessler's reagent, is a matter of controversy. A systematic study of its composition is in progress and will be the subject of our next communication.

EXPERIMENTAL

Mercuric iodide was purified by crystallizing from boiling ethyl alcohol, and dioxane by distillation after previous treatment with large excess of iodine and strong caustic potash solution. Other reagents used in the experiment, were of A.R. quality.

A 0.01M solution of iodine in aqueous dioxane was prepared and was used as the source of hypoiodite. Iodine solution (1 ml) was added to 50 ml of the solution which was previously introduced into each concentration cell during e.m.f. measurements .Thus an approximately 0.0002M solution of iodide and hypoiodite was formed from the iodine solution reacting with KOH present in the concentration cell. The iodide ion formed from iodine was regarded as negligible in comparison to iodide ion already present from other sources (see Tables I, II and III).

Caustic potash solutions of various strengths were prepared and standardized against hydrazine sulphate. The ionic strength of the solution was maintained at approximately 2.8 by adding the necessary quantity of potassium nitrate. These solutions were used throughout the experiment as solvent.

A solution of $[HgI_4]^{-2}$ (0.08M) was prepared by dissolving equivalent quantities of HgI_2 and KI in caustic alkali solution already prepared. The other dilute solutions of $[HgI_4]^{-2}$ were made by diluting with the same alkali solution. The solutions were then allowed to stand for 24 hours before any readings were taken. Potassium iodide solution of 0.1M was made by dissolving the required amount of KI in the caustic alkali solution and 0.01M solution by diluting with the same alkali solvent.

In all e.m.f. measurements, a Cambridge (portable type) pH-potentiometer was used. The iodide ion concentration of the $[HgI_4]^{-2}$ solution was calculated from the measured e.m.f. between the cells — in one of which, 50 ml of $[HgI_4]^{-2}$ solution, and in the other 50 ml of 0.1M KI solution were present. 1 Ml of iodine solution was added to each cell. The reference solution of 0.1M KI was checked against another solution of KI of 0.01M under identical conditions, and the e.m.f. observed was corrected accordingly. By varying the strength of KOH, two or more sets of data were obtained by following similar procedure. The values of apparent constant K', assuming $n = 2$ in (1), were also calculated. The results are given in the following tables.

TABLE I

$[B] = 1.63M$

A	E in volts (corrected)	pI	$p(A - \frac{I}{2})$	pK'_1
0.01	0.0235	1.78	2.77	2.87
0.02	0.0175	1.58	2.17	2.87
0.04	0.0125	1.42	1.68	2.88
0.08	0.0080	1.27	1.28	2.83

Av. = 2.86

TABLE II

$[B] = 0.84M$

A	E in volts (corrected)	pI	$p(A - \frac{I}{2})$	pK'_2
0.01	0.0255	1.85	2.53	3.32
0.02	0.0215	1.71	1.79	3.44
0.04	0.0175	1.58	1.57	3.47
0.08	0.0130	1.43	1.21	3.38

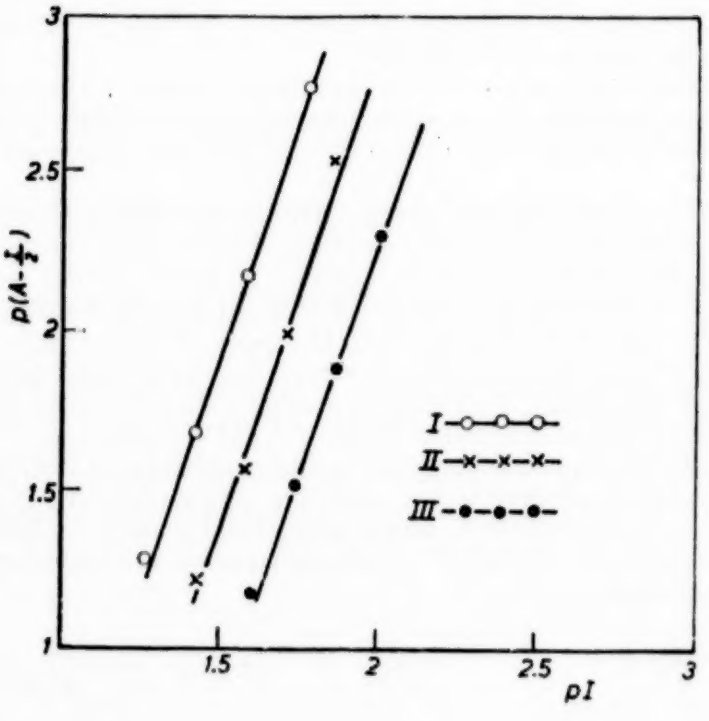
Av. = 3.40

TABLE III

$[B] = 0.43M$

A	E in volts (corrected)	pI	$p(A - \frac{I}{2})$	pK'_2
0.01	0.0300	2.00	2.30	4.00
0.02	0.0260	1.88	1.87	4.07
0.04	0.0225	1.75	1.51	4.04
0.08	0.0180	1.60	1.17	3.93

Av. = 4.01



Only a representative set of graphs has been given (Fig. 1) by plotting pI against $p(A - \frac{I}{2})$, *i.e.*, by assuming $n = 2$ in (1). The calculated as well as the theoretical values of slopes are given in Table IV.

TABLE IV

Graph No.	*Calculated values of slopes*	*Average value*	*Theoretical value*
I	3.00	2.95	3.00
II	2.94		
III	2.92		

The values of *m* were also calculated from the relation (5) and are given in a Table V.

TABLE V

Difference between	*Difference of pK' values*	*Difference of pB values*	*m*	*Average m*
I and II	0.54	0.29	1.86	1.98
I and III	1.15	0.58	1.98	
II and III	0.61	0.29	2.10	

TABLE VI

The equilibrium constant K as pK

pK'	*pB*	*pK = (pK' — 2 pB)*	*Average pK*
2.86	—0.21	3.28	3.26
3.40	0.08	3.24	
4.01	0.37	3.27	

SUMMARY

The nature of the reaction between $[\mathrm{HgI_4}]^{-2}$ and $\mathrm{OH^-}$ ions, which are the components of the Nessler's reagent, has been studied and established as $[\mathrm{HgI_4}]^{-2} + 2\,\mathrm{OH^-} \rightleftarrows \left[\mathrm{Hg}{}^{(\mathrm{OH})_2}_{\mathrm{I}_2}\right]^{-2} + 2\mathrm{I^-}$, by determining the concentration of iodide ions formed in the solution, potentiometrically from the concentration cells of iodide-hypoiodite system. The equilibrium constant has also been calculated and found to be $10^{-3.26}$.

RÉSUMÉ

La réaction entre les ions $[\mathrm{HgI_4}]^{-2}$ et $\mathrm{OH^-}$, les constituants du réactif de Nessler, a été étudiée; on est arrivé à l'équation $[\mathrm{HgI_4}]^{-2} + 2\mathrm{OH^-} \rightleftarrows \left[\mathrm{Hg}{}^{(\mathrm{OH})_2}_{\mathrm{I}_2}\right]^{-2} + 2\mathrm{I^-}$ par détermination potentiométrique de la concentration en ions iodhydriques formés dans la solution. La constante d'équilibre a été calculée, elle est égale à $10^{-3.26}$.

ZUSAMMENFASSUNG

Die Reaktion zwischen den $[\mathrm{HgI_4}]^{-2}$ und den $\mathrm{OH^-}$ Ionen, den Konstituenten des Nesslerschen Reaktivs wurde untersucht; man kann auf die Gleichung $[\mathrm{HgI_4}]^{-2} + 2\,\mathrm{OH^-} \rightleftarrows \left[\mathrm{Hg}{}^{(\mathrm{OH})_2}_{\mathrm{I}_2}\right]^{-2} + 2\mathrm{I^-}$, indem man die Konzentration der Jodid-Ionen, welche sich in der Lösung gebildet haben, potentiometrisch bestimmt. Die Gleichgewichtskonstante wurde gerechnet und ist gleich $10^{-3.26}$.

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AN ELECTROMAGNETIC VIBRATOR FOR ELECTRODES USED IN POLAROGRAPHY AND AMPEROMETRIC TITRATIONS

by

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Vibrating electrodes have been used in polarographic and amperometric determinations for several years and the devices employed to produce the necessary motion have varied considerably. Moving coil[1] and moving iron[2] (reed) loudspeaker units, cam-driven lever vibrators and electromagnetic vibrators[3] of the "massage" machine type have all been used. In the last mentioned publication the essential conditions for stable diffusion currents were established.

An electromagnetic vibrator of this type moves the electrode in approximately one direction, but may be disturbed and vibrate in other modes as well. The path of the electrode in its electrolyte may thus be altered and so cause difficulty in measuring accurately the amplitude of vibration. Also at the lower speeds of vibration, the diffusion current may change with change in the mode of vibration. However, such a vibrator has the advantages of being light and portable and gives a suitable amplitude of vibration when used on the a.c. mains for which it is designed.

The description which follows is of an electromagnetic vibrator designed with a centring guide to constrain the motion to one direction only.

The electromagnet is rigidly fixed within the cylindrical brass housing A and is connected to the current supply via the plug B on the top. A soft iron armature is held by strong flat spiral springs across the magnet and vibrates as the field changes. The electrode support is a brass rod screwed on to the armature and sliding freely in a collar which may be centred by means of three large nuts G. The electrode thus moves vertically up and down.

Figs. 1 and 2 are sectional drawings showing constructional details and Fig. 3 gives extra detail of the armature springs. These drawings with their legends should be self-explanatory and sufficient guide for construction of the apparatus.

The electrode, prepared as described previously[3,4,5] is screwed into the holder and the current supplied to the electromagnet adjusted by means of a "Variac" transformer to give a suitable amplitude of vibration. The amplitude is conveniently measured by focussing a microscope on a brightly illuminated bubble of air in the glass stem of the electrode. The conditions of vibration are more surely reproduced with this instrument[6] than with other types of apparatus.[7,8]

The author wishes to acknowledge the assistance of Mr. K. GUY in constructing the instrument.

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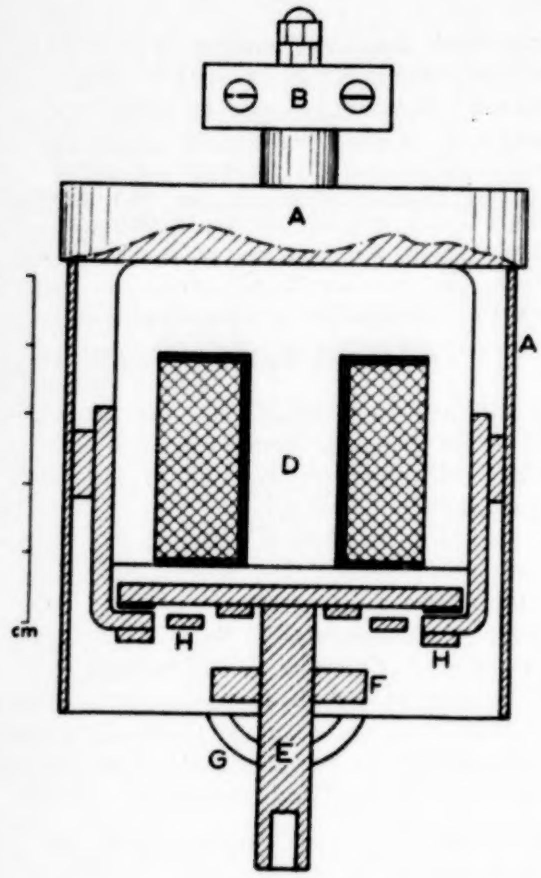

Fig. 1.

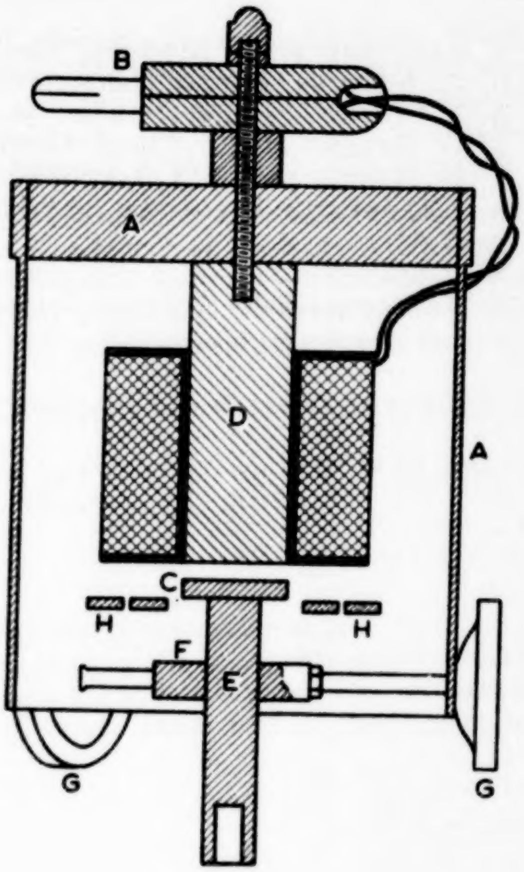

Fig. 2.

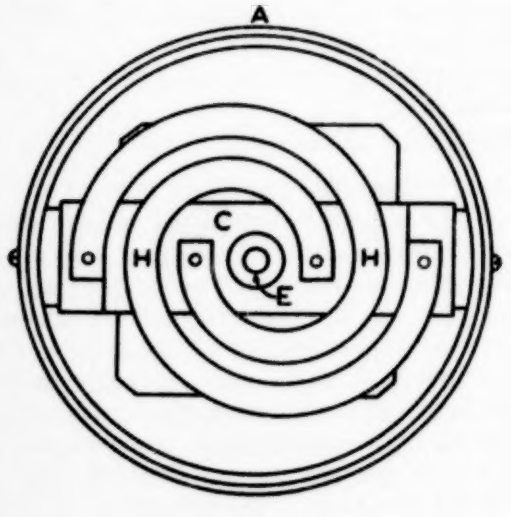

Fig. 3.

Scale drawing showing construction of the electromagnetic vibrator. A, cylindrical brass housing, B, mains plug, C, soft iron armature, D, laminated electromagnet with coil of about 8000 turns No. 36 S.W.G. enamelled copper wire, E, electrode support of brass rod, F, brass collar, G, control knobs for centring the electrode support, H, flat spiral springs of brass.

SUMMARY

Details of the construction of an electromagnetic vibrator for micro-electrodes are given. The design embodies a centring guide which constrains the vibration in one direction only. The instrument is suitable for polarography and amperometric titrations.

RÉSUMÉ

Des détails de construction d'un vibrateur électromagnétique pour microélectrodes sont donnés. Le dispositif permet les vibrations dans une direction seulement. Cet appareil convient à des titrations polarographiques et ampérométriques.

ZUSAMMENFASSUNG

Es sind Einzelheiten gegeben über die Konstruktion eines elektromagnetischen Vibrators für Mikroelektroden. Das Dispositiv erlaubt Vibrationen in nur einer Richtung. Dieser Apparat eignet sich für polarographische und amperometrische Titrationen.

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REVUE DE LIVRES

Handbuch der mikrochemischen Methoden, herausgegeben von F. Hecht und M. K. Zacherl, Wien. Band I/Teil 1: (Organisch-präparative und mikroskopische Methoden.) *Präparative Mikromethoden in der organischen Chemie,* von H. Lieb und W. Schöniger, Graz, 139 Abb. *Mikroskopische Methoden,* von L. Kofler † und A. Kofler, Innsbruck, 136 Abb., vi + 236 Seiten. Springer Verlag, Wien, 1954. Ganzleinen $ 11.30. Bei Abnahme d. ges. Hbd. Gln. $ 9.05.

L'extension que prennent, de nos jours, les techniques microchimiques avait rendu nécessaire la publication d'un recueil des progrès effectués dans ce domaine. L'honneur en appartient aux Autrichiens qui, avec le *Handbuch der mikrochemischen Methoden,* viennent ajouter aux grands traités encyclopédiques de la chimie un ouvrage dont l'utilité est évidente pour les chimistes d'aujourd'hui.

Cet ouvrage, dont la première partie du premier volume est déjà parue, traitera successivement les sujets suivants:

Vol. I, 2 — Méthodes biochimiques et médicales — Méthodes microchimiques appliquées aux denrées alimentaires.
Vol. II, 1 — Microméthodes radiochimiques — Mesure des rayons radioactifs en microchimie — Méthodes photographiques en radiochimie. (A paraître.)
Vol. II, 2 — Polarographie.
Vol. III — Méthodes d'analyse minérale.
Vol. IV — Méthodes d'analyse organique.
Vol. V — Méthodes de microdétermination des constantes physicochimiques.

Le volume I, 1 comprend la technique des méthodes de synthèse organique et celle des méthodes microscopiques. Toutes les techniques de la synthèse organique moderne et celles des déterminations faisant emploi du microscope y sont exposées avec une clarté extraordinaire et accompagnées de nombreuses illustrations et références bibliographiques.

Voici quelques chapitres de la première partie de ce volume:

IV. Extraction — 1. Extraction des corps solides
2. Extraction des liquides
3. Extraction fractionnée

VII. Distillation — 1. Distillation ordinaire
2. Distillation fractionnée
3. Dispositifs de fractionnement
4. Entraînement à la vapeur d'eau
5. Distillation moléculaire

Le lecteur trouvera dans cette partie la résolution de tous les problèmes qui peuvent le préoccuper concernant les appareillages à utiliser, même dans les cas les plus spéciaux. De plus, cet exposé est suivi de quelques tables d'intérêt pratique.

La deuxième partie du volume, consacrée à la technique microscopique, comprend onze chapitres traitant successivement la microdétermination du point de fusion, du poids moléculaire et de l'indice de réfraction, la microanalyse thermique, la cristallisation des corps organiques simples et celle de leurs mélanges ainsi que la cristallographie optique (emploi du microscope polarisant). Toutes ces questions, extrêmement importantes pour la chimie de synthèse moderne, sont abordées d'une manière très approfondie et qui ne laisse rien à désirer aux lecteurs.

En résumé, nous pouvons dire qu'il s'agit d'un livre indispensable à la plus grande partie des chimistes modernes et dont la place dans la littérature chimique mondiale est parmi des ouvrages tels que les Beilstein, les Gmelin, les Grignard, les Frésenius-Jander, etc. Nous ne pouvons donc que recommander vivement cet ouvrage qui est destiné à devenir un classique de son genre.

I. Kapetanidis (Genève)

Analyse Qualitative Rapide des Cations, par G. Charlot, D. Bézier et R. Gauguin, Dunod, Paris, 2e Edition, 1955, xii + 52 p., 5 fig., 450 Fr. fr.

Dans cet ouvrage les auteurs présentent une nouvelle édition de leur Méthode qualitative d'analyse rapide, parue en 1943. Cette méthode offre, sur l'édition précédente, certaines améliorations importantes, notamment dans la recherche des ions alcalino-terreux et alcalins. Par un emploi judicieux des complexons, les auteurs réussissent à éviter les séparations nécessitées dans l'édition précédente.

La méthode de Charlot c.s. offre, sur la méthode classique à l'hydrogène sulfuré, de nombreux avantages, par le fait qu'elle est extrêmement rapide, que l'ordre de recherches des ions est libre et par le fait que les quantités requises pour l'analyse sont à l'échelle semimicro ou microchimique.

Cet ouvrage intéressera tous ceux qui désirent se tenir au courant des progrès de la chimie minérale qualitative.

J. Hoste (Gand)

UNION INTERNATIONALE DE CHIMIE PURE ET APPLIQUEE

SECTION DE CHIMIE ANALYTIQUE

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

ANALYTICAL SECTION

ANNOUNCEMENT

Professor I. M. **Kolthoff**, President of the Analytical Section of the International Union of Pure and Applied Chemistry, has announced that the Congress on Analytical Chemistry to be held in Lisbon, September 9 through 16, 1956, will be under the patronage of the International Union of Pure and Applied Chemistry. Prof. **Fernando Pires de Lima**, Minister of Education, has appointed Professor D. **Antonio Pereira Forjaz** to be President of the Organizing Committee. Arrangements for the meeting are in the hands of Prof. **Pierre A. Laurent**, Instituto Superior Tecnico, Avenida Rovisco Pais, Lisbon, Portugal. Inquiries regarding plans for the meeting should be directed to him. It is intended that the Congress shall cover broadly all aspects of analytical chemistry. Further details will be published as soon as they become available.

S. E. Q. Ashley
Secretary,
Analytical Section UIPAC

TO WHOM IT MAY CONCERN

Dear Colleague,

The next International Congress of Analytical Chemistry to take place within the framework of activities of the International Union of Pure and Applied Chemistry will be held in Lisbon, from 9 to 16 September 1956, and I am very glad on behalf of the Organizing Committee to take advantage of this opportunity to invite you cordially to take part in this Congress, the first to be held in Portugal in the field of Chemistry.

Should you wish to contribute to the success of the Congress by presenting a paper on your particular subject, it would give us great pleasure.

I should be grateful if, in the meantime, you would give the names and addresses of individuals or firms which might be interested in having further details. For circulars and entry forms please apply to the undersigned.

We should like to include as many members as possible and it is in this connection that your help would be particularly valuable to us.

I look forward to receiving your reply and, in the hope that I shall have the pleasure of meeting you in Lisbon in 1956,

I am, on behalf of the Organizing Committee

Yours sincerely,

Pierre A. Laurent

Instituto Superior Técnico
Avenida Rovisco Pais
Lisboa (Portugal)

THE APPLICATION OF THIOSALTS IN ANALYSIS
III. A NEW SCHEME OF QUALITATIVE ANALYSIS — Part C

by

I. K. TAIMNI AND G. B. S. SALARIA

Chemical Laboratories, University of Allahabad, Allahabad (India)

In parts A and B of this paper[1,2] a new scheme of qualitative analysis, based on the formation of thiosalts of certain elements with concentrated ammonium sulphide, was put forward. Further investigations and experience with the working of the scheme in practical classes have shown that the scheme can be improved and the qualitative analysis of inorganic mixtures made more convenient and expeditious by incorporating certain modifications in the proposed scheme. The following changes are proposed for this purpose.

(1) Modification of Procedure II

Substitution of 1*N* sodium sulphide for concentrated ammonium sulphide.

In this procedure it was proposed to separate the elements which form thiosalts by adding excess concentrated ammonium sulphide to the solution containing all the basic radicles. The use of concentrated ammonium sulphide was found to be somewhat inconvenient on account of the fumes produced on neutralization with concentrated hydrochloric acid. This could be avoided to a great extent by adding the acid by means of a pipette, keeping the nozzle of the pipette below the surface of the solution, but further investigation showed that concentrated ammonium sulphide could be replaced by 1*N* sodium sulphide reagent with very satisfactory results. The following facts should be noted in this connection.

(a) When concentrated ammonium sulphide is used for forming the thiosalts some cadmium passes into the filtrate owing to the formation of the ammonia complex. With 1*N* sodium sulphide the precipitation of cadmium is complete.

(b) The thiosalt of platinum is formed more easily with 1*N* sodium sulphide than with concentrated ammonium sulphide. It is not necessary to treat the precipitate of hydroxides and sulphides with the sulphide reagent once again to ensure the complete solution of platinum sulphide.

(c) Mercuric sulphide is soluble in dilute solutions of sodium sulphide but if 2-4 g of ammonium acetate are added along with sodium sulphide reagent mercury is completely precipitated as sulphide. Mercury therefore forms part of the copper group when 1N sodium sulphide is used instead of concentrated ammonium sulphide.

(d) Antimonous and stannous sulphides are also liable to be precipitated from their thiosalts if ammonium acetate is added along with sodium sulphide, but their precipitation can be prevented by adding a larger excess of the sodium sulphide reagent. As the mixture is treated with concentrated nitric acid in *Procedure I* both antimony and tin will be present in their higher state of oxidation and therefore there is no possibility of the precipitation of their sulphides owing to the presence of ammonium acetate.

(e) Sodium carbonate precipitates barium, strontium and calcium completely and magnesium incompletely in presence of ammonium salts. If this salt is also added along with sodium sulphide and ammonium acetate in *Procedure II* all the barium, strontium and calcium will be precipitated along with the hydroxides and sulphides irrespective of whether any interfering acid is present in the mixture or not, and the possible distribution of these metals between the precipitate and the filtrate will be avoided. The solution of the thiosalts will under these conditions contain only part of the magnesium and alkalis. As salts of sodium have been introduced into this solution this metal will have to be tested for in a separate portion of the mixture.

The modified *Procedure II* will thus be as follows: — The acid solution containing the basic radicles is treated with 1N sodium sulphide reagent in excess (about 20 ml more of the reagent being generally required after the acid has been neutralized), 2-4 g ammonium acetate and 2 g of sodium carbonate. The mixture is stirred thoroughly and filtered. The precipitate is washed thoroughly with water, the washings being added to the filtrate. The precipitate contains the hydroxides and sulphides of metals like mercury, lead, titanium and zirconium and the filtrate the thiosalts of metals like arsenic, tin, molybdenum as well as magnesium and alkalis.

(2) Modification of Procedure III

It is necessary to introduce a few modifications in *Procedure III* in order to make the analysis of the group more convenient and accurate. In the first place, small quantities of nickel always pass into the filtrate after treatment of the solution with sodium sulphide reagent in *Procedure II*. On boiling the filtrate with concentrated hydrochloric acid this nickel is precipitated as NiS, together with the sulphides of the arsenic group. This nickel sulphide seems to be of the γ-variety[3] as it does not dissolve in 6N hydrochloric acid. It dissolves however in concentrated hydrochloric acid and potassium chlorate together with the other sulphides and the solution can be tested for nickel at any stage by means of dimethylglyoxime. In the second place, tellurium is precipitated completely by magnesia mixture as magnesium tellurite together with magnesium ammonium arsenate. The precipitate obtained with magnesia mixture has therefore to be tested not only for arsenic but also for tellurium. And lastly, the reduction of gold by means of oxalic acid takes place very slowly. Gold can be tested for far more conveniently by means of caustic soda and hydrogen peroxide.

The modified procedure for the analysis of the arsenic group is given in the following table.

ANALYSIS OF THE ARSENIC GROUP

(Precipitate obtained in *Procedure III*)

The precipitate may contain PtS_2, Au_2S_3, TeS_2, As_2S_5, SeS_2, MoS_3, V_2S_5 and NiS. The precipitate is boiled with concentrated hydrochloric acid and potassium chlorate, the solution evaporated and crystallized.

Ppt. $K_2[PtCl_6]$	Filt. $AuCl_3\,2H_2O$, H_2TeO_3, H_3AsO_4, H_2SeO_3, H_2MoO_4, H_3VO_4 and $NiCl_2$. Make it just alkaline with NaOH and add hydrogen peroxide, acidify with dilute hydrochloric acid, boil and filter. ($Ni(OH)_2$ is precipitated by NaOH but dissolves on treatment with HCl.)

Ppt. Brown or black. Au	Filt. H_2TeO_3, H_3AsO_4, H_2SeO_3, H_2MoO_4, H_3VO_4 and $NiCl_2$. Make the solution alkaline with concentrated ammonia, add magnesia mixture and filter

Ppt. $Mg(NH_4)AsO_4$ and $MgTeO_3$ Dissolve in HCl, add Na_2SO_3, boil and filter.	Filt. $(NH_4)_2SeO_3$, $(NH_4)_2MoO_4$, $(NH_4)_3VO_4$ and $[Ni(NH_3)_6]\,Cl_2$. Reduce the solution with Na_2SO_3 in presence of conc. HCl(7*N*) and filter.

Ppt. Black Te	Filt. H_3AsO_3 Add Na_2S and HCl successively. A yellow ppt. As_2S_3 shows As	Ppt. red or black Se	Filt. H_2MoO_4, H_3VO_4, $NiCl_2$ Divide the solution in 3 parts

Part I	Part II	Part III
Add NH_4CNS and Zn red solution Mo	Add H_2O_2 orange red colour V	Add dimethylglyoxime and make alkaline with ammonia A red coloration or ppt. Ni

(3) *Modification of Procedure V*

Complete separation of thallium with the copper group.

On treating the precipitate of hydroxides and sulphides with cold 1*N* hydrochloric acid in *Procedure V* thallium divides itself between the precipitate and the filtrate and has therefore to be tested for both in the copper and the iron groups. It has been found possible to make the thallium go completely with the copper group by adding potassium iodide to the mixture after treatment with 1*N* hydrochloric acid. The thallium in the solution is precipitated completely as thallous iodide and is filtered off with the sulphides of the copper group. The test for thallium in the iron group can then be omitted.

(4) *Modification of Procedure VII*

In *Procedure VII* it is recommended that the precipitate containing the hydroxides of the iron group as well as cerium and thorium be dissolved in concentrated hydrochloric acid and the cerium and thorium then separated from the iron group by means of oxalic acid in 0.5*N* hydrochloric acid solution. Further investigation has shown that this lengthy procedure may be eliminated altogether and cerium and thorium tested for along with the metals of the iron group by adopting the following modified procedure. This method of analysis also eliminates the possibility of calcium being precipitated as calcium oxalate in presence of 0.5*N* hydrochloric acid in case it is present in large amount.

ANALYSIS OF IRON AND CERIUM GROUPS

(Precipitate obtained in *Procedure VI*)

The precipitate from *Procedure VI* is dissolved in concentrated nitric acid and boiled with potassium chlorate to decompose oxalic acid (precipitated with alkaline earths) and precipitate manganese. Filter through asbestos.

<table>
<tr><td rowspan="4">Ppt. MnO_2</td><td colspan="5">Filt. Nitrates of Fe, Ti, Zr, Ce, Th and alkaline earths. Test for phosphate. Test for iron in a small portion and eliminate phosphate if it is present from the remaining solution as $FePO_4$ by adding $FeCl_3$ to acetate solution. Boil and filter hot. If phosphate is absent add NH_4OH in excess and filter. As zirconium and titanium are not quite completely precipitated in the procedure for elimination of phosphate, the filtrate is treated after elimination of phosphate, with excess of NH_4OH, boiled and filtered for complete precipitation of these two elements.</td></tr>
<tr><td colspan="4">Ppt. Basic acetates, hydroxides and phosphates of Fe, Ti, Zr, Ce and Th. If phosphate is present and has been eliminated no zirconium can be present in this precipitate. All the zirconium will be found in such a case in the insoluble residue in *Procedure I*. Dissolve the precipitate in concentrated nitric acid and add H_2O_2 in sufficiently large excess.</td><td rowspan="3">Filt. Acetates and chlorides of alkaline earths. Test for Ba, Sr, Ca and Mg as usual</td></tr>
<tr><td rowspan="2">(a) A yellow to orange colour in solution shows the presence of Ti</td><td rowspan="2">(b) To solution (a) add Na_2HPO_4 (1-2 g) heat to 60°-70° C, allow to stand for ½ hour. A white gelatinous precipitate of $Zr(HPO_4)_2$ shows Zr</td><td colspan="2">(c) Divide the filtrate from $Zr(HPO_4)_2$, if any, into two parts</td></tr>
<tr><td>Part I
Add KIO_3. A white ppt. shows presence of Th</td><td>Part II
Add Na_2SO_3 to reduce Ti. Boil with PbO_2. A yellow colour in supernatant liquid shows Ce</td></tr>
</table>

SUMMARY

1. Several modifications for improving the efficiency of the new scheme of qualitative analysis have been proposed.

2. It has been shown that 1*N* sodium sulphide is a more efficient and convenient reagent and may be substituted for concentrated ammonium sulphide.

3. If sodium carbonate is added along with sodium sulphide, barium, strontium and calcium are precipitated completely with the sulphides and hydroxides and the division of these metals into two groups is prevented.

4. It has been shown that the tedious separation of cerium and thorium from the iron group by means of oxalic acid is unnecessary and these metals can be tested for conveniently with the metals of the iron group.

5. The division of thallium into the iron and copper groups can be avoided and the metal precipitated completely with the copper group by adding potassium iodide in the treatment with 1*N* hydrochloric acid.

6. Modified procedures have been provided for the detection of nickel, tellurium and gold.

RÉSUMÉ

1. Plusieurs modifications ont été proposées pour améliorer la méthode d'analyse qualitative.

2. Il est démontré que le sulfure de sodium *N* peut remplacer avantageusement le sulfure d'ammonium en solution concentrée.

3. Si le carbonate de sodium est ajouté en même temps que le sulfure de sodium, les carbonates de baryum, strontium et calcium sont précipités quantitativement avec les sulfures et les hydroxydes; la séparation de ces éléments en deux groupes est évitée.

4. Il est démontré que l'ennuyeuse séparation du cérium et du thorium d'avec les éléments du groupe du fer, au moyen d'acide oxalique est inutile. Le cérium et le thorium peuvent être décelés en présence des éléments du groupe du fer.

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5. Le passage du thallium dans les deux groupes du fer et du cuivre peut être évité. Le thallium précipite complètement avec le groupe du cuivre par addition d'iodure de potassium lors de la précipitation à l'acide chlorhydrique *N*.

6. Des modifications ont été apportées à la détection du nickel, du tellure et de l'or.

ZUSAMMENFASSUNG

1. Mehrere Modifikationen wurden vorgeschlagen, um die qualitative Analyse zu verbessern.

2. Es wird gezeigt, dass das Natriumsulfid *N* das Ammoniumsulfid in konzentrierter lösung vorteilhaht ersetzt.

3. Wenn das Natriumkarbonat gleichzeitig mit dem Natriumsulfid dazugegeben wird, werden das Barium-, Strontium- und das Kalziumkarbonat quantitativ mit den Sulfiden und den Hydroxyden ausgefällt. Die Abtrennung dieser Elemente in zwei Gruppen wird ausgeschaltet.

4. Es wird gezeigt, dass die langweilige Abtrennung von Cerium und Thorium von den Elementen der Eisengruppe mit Hilfe von Oxalsäure unnütz ist. Das Cerium und das Thorium können in Gegenwart von Elementen der Eisengruppen gefunden werden.

5. Der Übergang des Thalliums in die Eisen und Kupfergruppe kann vermieden werden. Das Thallium fällt vollständig mit der Kupfergruppe aus, durch Zugabe von Kaliumiodid während der Ausfällung mit Salzsäure *N*.

6. Es wurden Modifikationen gebracht zur Auffindung von Nickel, Tellur und Gold.

REFERENCES

[1] I. K. Taimni and R. P. Agarwal, *Anal. Chim. Acta*, 9 (1953) 208.

[2] I. K. Taimni and R. P. Agarwal, *ibid.*, 9 (1953) 216.

[3] A. Thiel and H. Ohl, *Z. anorg. Chem.*, 61 (1909) 396; A. Thiel and H. Gessner, *ibid.*, 86 (1914) 1.

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NACHWEIS VON CHLORANIL IN DER TÜPFELANALYSE

VON

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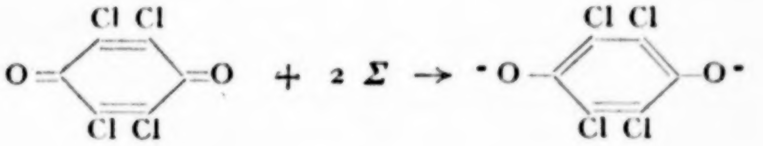
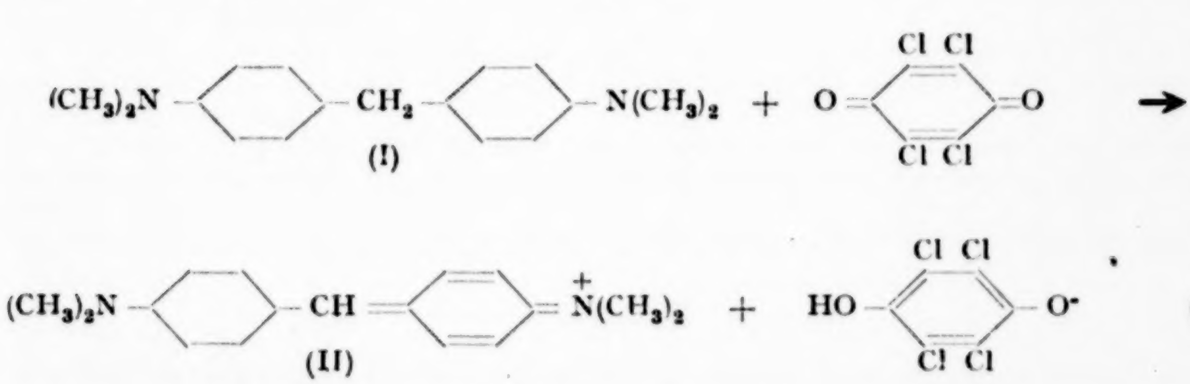
Das sog. Chloranil (Tetrachlor-*p*-benzochinon) ist ein starkes Oxydationsmittel durch den Übergang in Tetrachlorhydrochinon:



Demgemäss bewirkt Zusatz einer wässerig-alkoholischen Lösung von Chloranil zu angesäuerten Lösungen von Alkalibromid oder Jodid die sofortige Abscheidung von Brom bzw. Jod, die Oxydation von Sulfit zu Sulfat *etc.*

Da Chloranil in Äther ausgezeichnet löslich ist, wurde versucht, durch eine charakteristische Redoxreaktion mit einer ätherlöslichen organischen Verbindung zu einem selektiven Nachweis von Chloranil zu gelangen. Als Partner wurde die farblose ,,Tetrabase" (*p*-Dimethylaminodiphenylmethan I) gewählt, die bekanntlich zu dem tiefblauen chinoiden Diphenylmethanfarbstoff II oxydierbar ist[1]. Überraschenderweise tritt die erwartete Redoxreaktion 1 in ätherischer Lösung nicht ein. Bringt man jedoch einen Tropfen der farblosen oder schwach gelb-hellgrünen Lösung auf Filterpapier oder auf eine Tüpfelplatte, so hinterbleibt nach Verdunsten des Äthers ein tiefblauer Rückstand. Das gleiche Verhalten wurde beobachtet, wenn Chloroform, Benzol *etc.* als gemeinsames Lösungsmittel verwendet wird.



(1)

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Es lässt sich noch nicht mit Sicherheit angeben, worauf die hier beobachtete Reaktionslosigkeit des Chloranils in organischen Lösungsmitteln zurückzuführen ist. Die Abwesenheit von Wasser dürfte nicht die Ursache sein, weil Schütteln der ätherischen Lösung mit Wasser keine Veränderung herbeiführt, trots der merklichen Löslichkeit von Wasser in Äther. Wahrscheinlicher ist die Annahme, dass Chloranil oder Tetrabase (oder beide Verbindungen) in Äther, Chloroform *etc.* stabile Solvate bilden, die nicht in die oben angeführte Redoxreaktion 1 eintreten. Falls diese Annahme zutrifft, dann hätten wir es hier mit einer bisher einzig dastehenden „Maskierung durch Solvatbildung" zu tun, die bei Verdunstung des Lösungsmittels durch den Zerfall der Solvate aufgehoben wird. Damit steht in Übereinstimmung, dass 1 als Festkörperreaktion durch blosses Verreiben von trockenen Chloranil und Tetrabase sofort zustande kommt.

Die Redoxreaktion von Chloranil und Tetrabase bei Anwesenheit von flüchtigen organischen Lösungsmitteln ermöglicht einen selektiven Nachweis von Chloranil in Form einer Tropfenreaktion. Chinon zeigt die Reaktion nicht, hingegen dürfte das gleiche Verhalten bei Bromanil und organischen Perverbindungen zu erwarten sein.

Arbeitsweise

Eine geringe Menge der festen Probe oder ein Tropfen ihrer Lösung in Äther, Benzol etc. wird in die Vertiefung einer Tüpfelplatte gebracht. Ein Tropfen einer ätherischen Lösung von Tetrabase wird zugesetzt und mit einem Glasstab verrührt. Nach Verdunsten des Lösungsmittels hinterbleibt ein blauer Niederschlag. Es kann auch ein Tropfen der ätherischen Probelösung auf Filterpapier gebracht werden, das vorher mit ein bis zwei Tropfen der Reagenslösung angetüpfelt worden ist. Je nach der Menge des anwesenden Chloranils hinterbleibt nach Verdunsten des Äthers ein dunkelblauer bis hellblauer Fleck. Anblasen mit heißer Luft (Föhn) ist empfehlenswert.

Erfassungsgrenze:	0.25 γ Chloranil
Verdünnungsgrenze:	1:250,000

Reagens. 1%-ige Lösung von Tetrabase in Äther.

VERWENDUNG DES NACHWEISES VON CHLORANIL FÜR VORPROBEN

In der qualitativen organischen Analyse sind schnell ausführbare Vorproben sehr nützlich, die Hinweise über An-oder Abwesenheit bestimmter Verbindungsklassen geben, wodurch für weitere Prüfungen oft wichtige Anhaltspunkte gewonnen werden. Da bekanntlich verschiedene aromatische Verbindungen bei Erwärmung mit Kaliumchlorat und konz. Salzsäure als stabile Endprodukte Chloranil bilden[2,3], das wie oben beschrieben mit Tetrabase nachweisbar ist, so wurde versucht, darauf eine Vorprobe zu begründen, die in der Arbeitsweise der Tüpfelanalyse ausführbar ist.

Die Bildung von Chloranil aus aromatischen Verbindungen beruht auf Chlorierung, Oxydation, mitunter auch oxydativer Aufspaltung, die zweifellos nicht direkt, sondern über noch unbekannte Zwischenstufen verlaufen. An diesen Teilprozessen sind die gasförmigen Reaktionsprodukte beteiligt, die bei Erwärmung von Kaliumchlorat mit konz. Salzsäure entstehen:

$$HClO_3 + 5HCl \rightarrow 3H_2O + KCl + 3Cl_2 \qquad (2)$$

$$4HClO_3 \rightarrow 4ClO_2 + O_2 + 2H_2O \qquad (3)$$

Da durch den Ablauf von 2 und 3 Chlorat bzw. Chlorsäure vollständig zersetzt wird, so kann etwa gebildetes Chloranil durch Zusatz von Kaliumjodid (Jodbildung) oder nach Extraktion mit Äther durch die Redoxreaktion mit Tetrabase nachgewiesen werden. Nach unseren Beobachtungen ist der zweite Weg zuverlässiger.

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Arbeitsweise. In einer Mikroeprouvette wird ein Tropfen der Probelösung oder eine kleine Menge der festen Substanz mit einem Tropfen Kaliumchloratlösung und einem Tropfen Salzsäure versetzt und solange erwärmt, bis kein Chlor entweicht. Nach Erkalten werden 2-3 Tropfen Wasser zugesetzt und mit 5-10 Tropfen Äther ausgeschüttelt. Nach Trennung der Äther-Wasser-Schichten werden ein bis zwei Tropfen der ätherischen Lösung auf Filterpapier gebracht und der Tüpfelfleck mit einem Tropfen einer ätherischen Lösung der Tetrabase angetüpfelt. Nach Verdunsten des Äthers (Föhn) hinterbleibt ein blauer Fleck bei Anwesenheit solcher aromatischer Verbindungen, die zu Chloranil oxydativ aufspaltbar sind.

Reagenzien. 1. Gesättigte wässerige Lösung von Kaliumchlorat
2. Konz. Salzsäure
3. 1%-ige ätherische Lösung von Tetrabase

Das Verfahren wurde bei nachfolgenden Verbindungen in Milligramm-Mengen überprüft. Bei starkem Ausfall der Chloranilreaktion wurde in vielen Fällen die Erfassungsgrenze ermittelt.

I. Starker Ausfall der Chloranil-Reaktion

Acetanilid; Benzidin (0.5 γ); *p*-Chloranilin (0.5 γ); Cumarin; Diphenylamin (0.25 γ); Emetin; *m*-Hydroxybenzaldehyd; *p*-Hydroxybenzaldehyd (0.25 γ); 8-Hydroxychinolin; *p*-Hydroxydiphenyl; Isatin (1 γ); Methylenblau (1 γ); Mercaptobenzthiazol (10 γ); *α*-Naphtol (10 γ); *β*-Naphtol (10 γ); *α*-Naphtylamin (5 γ); *α*-Naphtylaminchlorhydrat; Natrium-dihydroxybenzolsulfonat; *p*-Nitrophenol (0.5 γ); Papaverinchlorhydrat; Pentachlorphenol; Phenolphtalein (1 γ); Phenylharnstoff (10 γ); Pikrinsäure (5 γ); Chinon; Tryptophan; Salicin (2.5 γ); Salicylsäure (1 γ); Sulfametazin; Sulfanilsäure (0.5 γ); Sulfapyridin; Sulfathiazol; Sulfosalicylsäure (1 γ).

II. Schwacher Ausfall der Chloranil-Reaktion (in mg-Mengen)

Azobenzol; Ephedrin; Isochinolin; Kongorot; Nitrobenzol; *o*-Nitrobenzoesäure; Chinolin; Tetrabase; Toluol.

III. Keine Chloranil-Reaktion

Alizarin; Anthrachinon; Anthracen; Benzoesäure; Chromotropsäure; Codein; Curcumin; Ellagsäure; Hexachlorbenzol; Morin; Morphinchlorhydrat; Naphtalin; *α*-Nitrosonaphtol; Phtalsäure; Pyrogallol; Chinalizarin; Chininchlorhydrat; Saccharin; Sudan III.

Wie die unter I-III angegebenen Befunde zeigen, erfolgt bei Erwärmung mit Kaliumchlorat und konz. Salzsäure zwar bei sehr vielen, aber, wie bereits von COLMANT[3] beobachtet worden ist, keineswegs bei allen aromatischen Verbindungen die Bildung von Chloranil. Das hier beschriebene Verfahren ermöglicht daher keine entscheidende Vorprobe auf aromatische Verbindungen. Indessen lassen sich die Resultate der Chloranilprobe verwerten bei Vergleich mit der Vorprüfung auf aromatische Verbindungen nach LE ROSEN[4]. Bemerkenswert ist die Tatsache, dass Polyphenole, Hydroxyanthrachinon und Flavanole, aber auch so einfach gebaute Verbindungen wie Benzoesäure und Phtalsäure bei Erwärmung mit Kaliumchlorat und konz. Salzsäure kein Chloranil bilden. Es dürften daher wohl bestimmte Atomgruppen und Strukturmomente für die Bildung von Chloranil verantwortlich sein. Dies zeigt sich sehr deutlich im Verhalten von Naphtol- und Naphtylaminsulfonsäuren, wie nachfolgende Daten zeigen:

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1, 4	Naphtolsulfonsäure	starke	Chloranilreaktion	(5 γ)
1, 5	Naphtolsulfonsäure	keine	,, ,,	
2, 6	Naphtolsulfonsäure	positive	,, ,,	(50 γ)
2, 7	Naphtllsulfonsäure	schwache	,, ,,	(250 γ)
1, 3	Naphtylaminsulfonsäure	keine	,, ,,	
2, 6	Naphtylaminsulfonsäure	schwache	,, ,,	
1, 4	Naphtylaminsulfonsäure	positive	,, ,,	(50 γ)
2, 6, 8	Naphtoldisulfonsäure	keine	,, ,,	
1, 8, 3, 6	Dioxynaphtalindisulfonsäure	keine	,, ,,	
2, 3, 6	Naphtylamindisulfonsäure	keine	,, ,,	

Nach obigen Daten kann demnach die Chloranilreaktion bei Naphtol- und Naphtylaminsulfonsäure zur Charakterisierung bestimmter hierhergehöriger Verbindungen herangezogen werden.

Wir danken an dieser Stelle dem Conselho Nacional de Pesquisas für die Unterstützung bei der Durchführung dieser Arbeit.

ZUSAMMENFASSUNG

Bei Vereinigung von Chloranil und Tetrabase in ätherischer Lösung erfolgt keine Reaktion. Die Redoxreaktion, unter Bildung eines blauen Diphenylmethanfarbstoffes, tritt erst ein nach Verdunsten des Äthers. Auf diesem Effekt lässt sich ein selektiver Nachweis von Chloranil begründen, der als Tüpfelreaktion ausführbar ist, wobei eine Erfassungsgrenze von 0.25 γ Chloranil erreicht werden kann. Es wird eine Vorprobe auf aromatische Verbindungen beschrieben, die darin besteht, das Probematerial mit Kaliumchlorat und konz. Salzsäure zu erwärmen und hierbei gebildetes Chloranil durch Tetrabase nachzuweisen. Die Überprüfung von 71 Verbindungen hat gezeigt, dass nicht sämlichte aromatische Verbindungen in Chloranil überführbar sind, sondern dass charakteristische Ausnahmen bestehen.

SUMMARY

Mixing chloranil with tetrabase in ether solution gives no reaction. The redox reaction, with formation of a blue diphenylmethane dye, occurs only after evaporation of the ether. On this effect can be based a selective identification of chloranil. It can be carried out as a spot test showing an identification limit of 0.25 γ of chloranil. The authors describe a preliminary test for aromatic compounds, which consists in heating the test material with potassium chlorate and conc. hydrochloric acid and identifying the hereby formed chloranil by means of tetrabase. The investigation of 71 compounds has shown that not all aromatic compounds can be converted to chloranil, but that there exist characteristic exceptions.

RÉSUMÉ

Le mélange de chloranile et de tétraméthyldiamino-diphénylméthane, en solution éthérée ne donne pas de réaction. La réaction redox, avec formation d'un colorant bleu, se produit après évaporation de l'éther; elle peut être utilisée pour l'identification sélective du chloranile, par réaction à la touche; on peut arriver à une limite de sensibilité de 0.25 γ de chloranile. Les auteurs décrivent une recherche préliminaire de composés aromatiques consistant à chauffer le matériel d'essai avec du chlorate de potassium et de l'acide chlorhydrique concentré et à identifier le chloranile formé par la tétrabase. L'examen de 71 composés a montré que pas tous les composés aromatiques peuvent être transformés en chloranile, mais qu'il y a des exceptions caractéristiques.

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SIMPLE INSTRUMENT FOR TITRIMETRY WITHOUT INDICATORS GAS PRESSURE END-POINT TECHNIQUE

IX. IODOMETRY, IODIMETRY, IODATE AND PERIODATE TITRIMETRY

by

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In previous papers[1] a gas pressure technique to locate the end-point in volumetric analysis was developed. The outstanding feature of this technique is the fact, that solutions, which for some reason cannot be titrated to a visual end-point, can be titrated, frequently by standard methods, in a simple, inexpensive instrument.

The aim of the present communication is to extend the applicability of the technique to several oxidation reduction titrations.

An easily assembled glass instrument for gas pressure end-point titrations was described in the previous paper cited.

IODOMETRY

Any oxidizing agent which liberates quantitatively iodine from potassium iodide can be determined with standard hydrazine or arsenious oxide solution using the gas pressure end-point technique.

(a) Hydrazine reacts with iodine rapidly and quantitatively:

$$N_2H_4 + 2I_2 \rightarrow N_2 + 4HI \qquad (1)$$

if the pH of the solution is maintained between 7 and 7.4. At a lower pH the reaction is quantitative, but very slow. At a greater pH the results are not accurate[2]. Sodium hydrogen phosphate or sodium bicarbonate can be used as buffer. In the former case the end-point is reached when gas evolution, due to reaction 1, ceases. In the latter case the reaction proceeds as follows:

$$N_2H_4.H_2SO_4 + 2I_2 + 6NaHCO_3 \rightarrow N_2 + 6CO_2 + 4NaI + Na_2SO_4 + 6H_2O \qquad (2)$$

Once all the iodine has been consumed, the gas evolution will be due only to the reaction:

$$N_2H_4.H_2SO_4 + 2NaHCO_3 \rightarrow 2CO_2 + N_2H_4 + Na_2SO_4 + 2H_2O \qquad (3)$$

The diminution of the gas volume given off per drop of standard solution is easy to perceive and serves to locate the end-point.

Reagents

Standard 0.05*M* hydrazine sulfate solution. Dissolve 6.5062 g of c.p. $N_2H_4.H_2SO_4$ in water and dilute to the mark of a 1000 ml volumetric flask.

Concentrated sodium hydrogen phosphate solution whose pH was adjusted to 7.0-7.5, solid sodium bicarbonate or concentrated solution containing equal parts by weight of borax and boric acid.

Procedure 1

Transfer 5.00 to 10.00 ml of the iodine-containing sample solution to the titration flask and add a sufficient amount of buffer. While stirring the mixture by means of the magnetic stirrer, titrate with standard hydrazine sulfate solution. Approaching the end-point wait until nearly all the gas has been expelled, then proceed as follows: Close the apparatus, introduce one drop of standard solution into the flask, observe the displacement of the liquid in the U-tube after one minute, open the instrument, close and repeat until the liquid in the U-tube no longer shows the regular increase in volume of the system.

(b) Arsenious oxide solutions are used currently in the standardization and determination of iodine by a visual end-point technique:

$$As_2O_3 + 2I_2 + 2H_2O \rightleftharpoons As_2O_5 + 4HI \tag{4}$$

This reaction is reversible and sodium bicarbonate is added to make it quantitative in the direction left to right:

$$4HI + 4NaHCO_3 \rightarrow 4CO_2 + 4NaI + 4H_2O \tag{5}$$

This standard method can be used in conjunction with the gas pressure end-point technique without modifications. The end-point is reached when gas evolution ceases.

Reagents

Standard $0.025M$ arsenious oxide solution. Dissolve 4.9455 g of c.p. As_2O_3 in 50 ml of warm, $2N$ sodium hydroxide solution, using a 1000 ml flask. Neutralize by the addition of sulfuric acid, using phenolphtalein as indicator. Dissolve 20 g of sodium bicarbonate in 500 ml of water, add this solution to the volumetric flask and dilute to the mark with water.

Procedure 2

Transfer 5.00 to 10.00 ml of the neutral iodine containing sample solution to the titration flask. While stirring the mixture by means of the magnetic stirrer, titrate with standard arsenite solution, which contains bicarbonate, using the instructions given in *Procedure* 1 to locate the end-point.

IODIMETRY

A standard iodine solution is used to determine certain reducing substances by direct visual end-point titration. In all reactions involved the iodine is reduced to hydroiodic acid. Since many of the titrations have to be or can be performed in bicarbonate buffered solutions, they are accompanied by carbon dioxide evolution. For instance:

$$Na_2HAsO_3 + 2NaHCO_3 + I_2 \rightarrow 2CO_2 + Na_2HAsO_4 + 2NaI + H_2O \tag{6}$$

Thus a direct titration is possible also using the gas pressure technique to locate the end-point. If a phosphate or borate buffer is used, an excess of iodine solution must be added to the sample and back-titrated with standard hydrazine solution (see iodometry).

Reagents

Standard $0.05M$ iodine solution. Dissolve 12.7 g of iodine and 40 g of potassium iodide in 25 ml of water and dilute to 1 liter. Standardize against arsenious oxide solution.

Solid sodium bicarbonate.

Procedure 3

Transfer 5.00 to 10.00 ml of the neutral sample solution to the titration flask and add a sufficient amount of solid sodium bicarbonate. While stirring the mixture by means of the magnetic stirrer, titrate with standard iodine solution, using the instructions given in *Procedure* 1 to locate the end-point.

IODATE TITRIMETRY

A standard iodate solution is used to determine certain reducing substances by direct visual end-point titration. If the particular redox reaction liberates a gas rapidly and quantitatively, a direct titration is also possible using the pressure end-point technique. If the reaction is not accompanied by gas evolution, an excess standard iodate solution can be added to the sample and back-titrated with standard hydrazine solution until gas evolution ceases.

The method can be applied to acid or to alkaline solutions. At a pH lower than 7 the following reaction takes place:

$$5N_2H_4 + 4KIO_3 + 4H^+ \rightarrow 2I_2 + 5N_2 + 4K^+ + 12H_2O \qquad (7)$$

Reaction 1, which is very slow in acid solution, does not interfere. At a pH higher than 7 the reaction is represented by the sum of reactions 7 and 1:

$$3N_2H_4 + 2KIO_3 \rightarrow 3N_2 + 2KI + 6H_2O \qquad (8)$$

In neutral medium hydrazine reacts only slowly with iodate.

Reagents

Standard 0.1*M* potassium iodate solution. Dissolve 21.402 g of c.p. potassium iodate in water and dilute to the mark of a 1000 ml volumetric flask.

Standard 0.1*M* hydrazine sulfate solution. Dissolve 13.012 g of c.p. $N_2H_4.H_2SO_4$ in water and dilute to the mark of a 1000 ml volumetric flask.

Hydrochloric or sulfuric acid, approx. 6*N* solution.

Sodium hydroxide, approx. 3*N* solution.

Procedure 4

Transfer 5.00 to 10.00 ml of the iodate-containing solution to the titration flask and add an equal volume of the 6*N* acid (or the 3*N* hydroxide) solution. Stirring the mixture by means of the magnetic stirrer, titrate with standard hydrazine solution, using the instructions given in *Procedure* 1 to locate the end-point.

PERIODATE TITRIMETRY

The use of periodic acid in the analysis of organic compounds and in the studies of their structure has become of increasing importance. An excess of periodic acid or periodate is employed:

$$IO_4^- + R^- \rightarrow IO_3^- + R.O^- \qquad (9)$$

and the excess determined by different methods, the most common involving reaction between arsenious acid and the periodate in presence of bicarbonate[3].

According to SMITH AND WILLEFORD[4], when flavonol and related compounds, such as quercitin, are treated with periodic acid, highly colored solutions are produced.

It is impossible to determine directly the amount of periodate consumed by these compounds, for the color of the solutions masks the starch iodine end-point on which the analytical method depends.

The gas pressure end-point technique makes possible the direct titration of the colored solutions by the standard methods. No additional operations, chemicals or special resins[4] for separation of the periodate from the reaction mixture are needed.

The following methods are available for use in the determination of periodic acid in presence of iodic acid:

1. The reduction of periodate by excess of sodium arsenite (catalyzed by iodide) in neutral solution buffered with excess sodium bicarbonate. The excess arsenite is titrated employing standard iodine solution.

This standard method can be used in conjunction with the gas pressure end-point technique without modification. The only point to be kept in mind is that, if any carbonate were formed in the periodate reduction by arsenite, as would be the case if neutral sodium para-periodate were used:

$$Na_2H_3IO_6 + AsO_3^{-3} + NaHCO_3 \rightarrow NaIO_3 + AsO_4^{-3} + Na_2CO_3 + 2H_2O \qquad (10)$$

the first quantities of iodine solution added would not give rise to gas evolution. Only when all of the sodium carbonate has been transformed to bicarbonate by hydroiodic acid, will gas evolution be noted. Consequently it is necessary to use a regular excess of arsenite in reaction 10. Twice the theoretical amount is sufficient.

Reagents

Standard 0.025*M* arsenious oxide solution (see above).
Standard 0.05*M* iodine solution (see above).
20% potassium iodide solution.

Procedure 5

Transfer 5.00 to 10.00 ml of the neutral periodate solution to the titration flask, add an accurately measured excess of the standard arsenite solution, which contains bicarbonate, and 1 ml of the potassium iodide solution. After 5 minutes at room temperature titrate the excess arsenite using a standard iodine solution (*Procedure* 3).

2. The reduction of periodate by excess iodide in neutral solution buffered with sodium bicarbonate[5]:

$$NaIO_4 + 2NaI + 2NaHCO_3 \rightarrow NaIO_3 + I_2 + 2Na_2CO_3 + H_2O \qquad (11)$$

The liberated iodine is titrated with arsenite.

No modifications are necessary to find the end-point in this standard method by the gas pressure technique. Theoretically, in the titration of the iodine formed in reaction 11 with arsenite, no gas evolution should be noted, since all the carbon dioxide formed should be used up in bicarbonate formation. In practice, however, due to the existence of much bicarbonate in the mixture, gas evolution begins before the end-point and the carbonate does not interfere with the method.

Reagents

Standard 0.025*M* arsenious oxide solution (see above).
Sodium bicarbonate, solid.
20% potassium iodide solution.

Procedure 6

Transfer 5.00 to 10.00 ml of the neutral periodate solution to the titration flask, add 0.1 to 0.2 g of sodium bicarbonate and an excess of potassium iodide solution. Titrate the liberated iodine with standard arsenite solution (*Procedure* 2).

3. The reduction of periodate by hydrazine in neutral solution buffered with boric acid-borate:

$$2NaIO_4 + N_2H_4 \rightarrow 2NaIO_3 + N_2 + 2H_2O \qquad (12)$$

Reagents

Standard 0.05*M* hydrazine sulfate solution (see above).
Concentrated solution containing equal parts by weight of borax and boric acid.

Procedure 7

Transfer 5.00 to 10.00 ml of the neutral periodate solution to the titration flask, add a sufficient amount of buffer solution and titrate with standard hydrazine sulfate solution, using the instructions given in *Procedure* 1 to locate the end-point.

Combining *Procedures* 7 and 4 it is possible to determine the periodate and the iodate content of the same sample. After conclusion of *Procedure* 7 (periodate content), the solution is made strongly acid (or alkaline) and the titration is continued to the end of the gas evolution (iodate content).

4. The reduction of periodate by hydrazine in acid solution results in the sum of reactions 12 and 7:

$$4NaIO_4 + 7N_2H_4 + 4H^+ \rightarrow 7N_2 + 2I_2 + 4Na^+ + 16H_2O \qquad (13)$$

In this method iodate also reacts with the titrant, but by means of a blank determination and a determination of the periodate-iodate mixture resulting from a given organic oxidation procedure (reaction 9), the amount of periodate reacted may be calculated.

The oxidation of hydrazine by periodate in acid solution yields neither hydrazoic acid nor ammonia[6].

Reagents

Standard 0.05*M* hydrazine sulfate solution (see above).
Sulfuric acid, approx. 6*N* solution.

Procedure 8

Transfer 5.00 to 10.00 ml of the periodate solution to the titration flask, add an equal volume of the sulfuric acid solution and titrate with the standard hydrazine solution, using the instructions given in *Procedure* 1 to locate the end-point.

Precision and accuracy

In the instances studied, precision is comparable with that which can be attained in normal indicator end-point titrations. The accuracy of every reaction described was proved, observing during the same titration the end-point by both the gas pressure and a standard visual end-point technique. In every instance the same drop of titrant which indicated the end-point by the gas pressure technique was also responsible for the color change of the solution.

Concentration limit

The considerations exposed in the previous paper under the same heading are valid.

DISCUSSION

Hydrazine sulfate can be obtained pure and anhydrous by recrystallization from water and drying at 140° C. Its solutions are stable indefinitely and can be standardized easily by titration with sodium hydroxide, using methyl red as indicator. It has been frequently recommended in the literature as a standard for alkalimetry, as well as for iodometry[7].

Its low oxidation potential makes it a very versatile reagent. Its reactivity varies with the pH of the sample solution and selective oxidations can be achieved varying this factor. It is a much stronger reducing agent in alkaline (than in acid) medium, being capable of reducing many metal salts. These interfere consequently with any method employing the reagent in alkaline solution. No analysis of a complex mixture should be attempted without consulting a complete survey of the reactions of hydrazine with oxidizing agents, such as the one given by AUDRIETH AND OGG[8].

Even though hydrazine can be made to react with all the common analytical oxidizing agents, not all the oxidations are sufficiently simple to be useful in titrimetry. In addition to nitrogen, appreciable quantities of ammonia and hydrazoic acid are often formed.

TABLE I

TITRATION OF IODINE SOLUTION WITH HYDRAZINE SOLUTION

ml 0.05M I_2 taken	*Addition to the I_2 solution*	*ml 0.05M $N_2H_4.H_2SO_4$ consumed* Procedure 1	Starch-iodine color end-point	Δ %
10.00	5 ml phosphate buffer	5.05		
10.00		5.03		
10.00		5.06		
		mean 5.05	mean 5.04	+0.2

TABLE II

TITRATION OF IODINE SOLUTION WITH ARSENITE SOLUTION

ml 0.05M I_2 taken	*ml 0.05M AsO_3^{-3} consumed* Procedure 2	Starch-iodine color end-point	Δ %
5.00	4.99		
5.00	4.98		
5.00	4.97		
	mean 4.98	mean 4.97	+0.2

TABLE III

TITRATION OF ARSENITE SOLUTION WITH IODINE SOLUTION

ml 0.05M AsO_3^{-3} *taken*	*Addition to the* AsO_3^{-3} *solution*	*ml 0.05M* I_2 *consumed*		Δ %
		Procedure 3	*Starch-iodine color end-point*	
5.00		5.05		
5.00	0.1 g $NaHCO_3$	5.02		
5.00		5.02		
		mean 5.03	mean 5.04	−0.2

TABLE IV

TITRATION OF IODATE SOLUTION WITH HYDRAZINE SOLUTION

ml 0.1000M KIO_3 *taken*	*Addition to the* KIO_3 *solution*	*ml 0.1000M* $N_2H_4.H_2SO_4$		Δ %
		consumed	*theoretical*	
4.00	5 ml 6*N* HCl	4.97		
4.00		4.98		
4.00		5.01		
4.00		4.99		
		mean 4.99	5.00	−0.2
4.00	5 ml 6*N* H_2SO_4	4.99		
4.00		5.00		
4.00		5.02		
		mean 5.00	5.00	0.0
4.00	5 ml 3*N* NaOH	6.03		
4.00		6.02		
4.00		5.99		
		mean 6.01	6.00	+0.2

TABLE V

DETERMINATION OF POTASSIUM PERIODATE BY TITRATION OF EXCESS ARSENITE WITH IODINE SOLUTION

ml KIO_4 *solution taken*	*Additions to the* KIO_4 *solution*	*ml 0.05M* I_2 *consumed*		Δ %
		Procedure 5	*Starch-iodine color end-point*	
5.00	5.00 ml 0.05*M* AsO_3^{-3}	2.75		
5.00	1 ml KI solution	2.72		
5.00		2.72		
		mean 2.73	mean 2.72	+0.4

TABLE VI

DETERMINATION OF POTASSIUM PERIODATE BY TITRATION OF IODINE EX-KI WITH ARSENITE SOLUTION

ml KIO_4 *solution taken*	*Additions to the* KIO_4 *solution*	*ml 0.05M* AsO_3^{-3} *consumed*		Δ %
		Procedure 6	*Starch-iodine color end-point*	
5.00	0.1 g $NaHCO_3$ 1 ml KI solution	2.27	2.27	0.0
10.00	0.2 g $NaHCO_3$ 2 ml KI solution	4.58	4.56	+0.4

TABLE VII

TITRATION OF POTASSIUM PERIODATE WITH HYDRAZINE SOLUTION

ml KIO_4 solution taken	*Additions to the KIO_4 solution*	*ml 0.05M $N_2H_4.H_2SO_4$ consumed*		*Δ %*
		Procedure 7		
5.00	5 ml borate buffer	1.13		—0.9
			starch-iodine color end-point	
5.00	5 ml borate buffer 1 ml 20% KI solution		1.14	
		Procedure 8	*calculated from starch-iodine color end-point*	
5.00	5 ml $6N$ H_2SO_4	4.02	$1.14 \cdot \frac{7}{2} = 3.99$	+0.8

SUMMARY

The present paper shows, that the gas pressure end-point technique can be applied to several oxidation reduction titrations. Iodometry, iodimetry, iodate and periodate titrimetry were studied. Standard arsenite, iodine and hydrazine sulfate solutions were used as titrants. The results are comparable in precision and accuracy to values obtained by the standard visual end-point titrations.

RÉSUMÉ

L'auteur démontre que la technique utilisant la pression gazeuse pour la détermination du point d'équivalence peut être appliquée à plusieurs titrations d'oxydo-réduction. L'iodométrie, l'iodimétrie, les titrations au moyen d'iodate ou de periodate ont été ainsi étudiées. Des solutions étalon d'arsenite, d'iode et de sulfate d'hydrazine ont été utilisées comme réactifs pour effectuer ces titrations. Les résultats peuvent être comparés, comme précision et comme exactitude, aux valeurs obtenues par les titrations à virages visuels.

ZUSAMMENFASSUNG

Der Autor zeigt, dass die Technik, mit Gasdruck den Gleichgewichtspunkt zu bestimmen, für mehrere Oxydo-Reduktion Titrationen angewendet werden kann. Die Iodometrie, Iodimetrie, die Titrationen mit Hilfe von Iodat oder Periodat wurden auf diese Weise untersucht. Man verwendete Vergleichslösungen von Arsenit, Iod und Hydrazinsulfat als Reaktive, um diese Titrationen durchzuführen. Die Resultate können in Bezug auf Präzision und Exaktheit mit den Werten, die man durch Titrationen mit sichtbaren Farbumschlägen erhält, verglichen werden.

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VOLUMETRIC STUDIES IN OXIDATION-REDUCTION REACTIONS
III. REDUCTION WITH FERROUS ETHYLENEDIAMINE SULPHATE
INDIRECT DETERMINATIONS*

by

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In this investigation an attempt has been made to determine indirectly potassium chlorate, potassium bromate, potassium metaperiodate, potassium dichromate, potassium ferricyanide, potassium permanganate, potassium persulphate, hydrogen peroxide and ceric sulphate by a volumetric method, using ferrous ethylenediamine sulphate, $FeSO_4.(CH_2.NH_3)_2SO_4.\ 4H_2O$, as a reducing agent.

In acid medium ferrous ethylenediamine sulphate reacts with these substances according to the following equations:

$$\begin{aligned}
ClO_3^- + 6\,Fe^{+2} + 6\,H^+ &= Cl^- + 6\,Fe^{+3} + 3\,H_2O \\
BrO_3^- + 6\,Fe^{+2} + 6H^+ &= Br^- + 6\,Fe^{+3} + 3\,H_2O \\
IO_4^- + 2\,Fe^{+2} + 2\,H^+ &= IO_3^- + 2\,Fe^{+3} + H_2O \\
Cr_2O_7^{-2} + 6\,Fe^{+2} + 14\,H^+ &= 2\,Cr^{+3} + 6\,Fe^{+3} + 7\,H_2O \\
2[Fe(CN)_6]^{-3} + 3\,Fe^{+2} &= Fe_3[Fe(CN)_6]_2 \\
MnO_4^- + 5\,Fe^{+2} + 8\,H^+ &= Mn^{+2} + 5\,Fe^{+3} + 4\,H_2O \\
S_2O_8^{-2} + 2\,Fe^{+2} &= 2\,SO_4^{-2} + 2\,Fe^{+3} \\
O_2^{-2} + 2\,Fe^{+2} + 4\,H^+ &= 2\,Fe^{+3} + 2\,H_2O \\
Ce^{+4} + Fe^{+2} &= Ce^{+3} + Fe^{+3}
\end{aligned}$$

EXPERIMENTAL

Ferrous ethylenediamine sulphate was prepared by the method of CARAWAY AND OESPER[1].

A known weight of each substance was mixed with an excess of standard ferrous ethylenediamine sulphate solution and the mixture acidified with sulphuric acid to keep its normality between 1 and 2*N*. Phosphoric acid mixture was used in the case of potassium chlorate, potassium bromate, potassium ferricyanide and potassium persulphate. 5 to 10 ml of Zimmermann's reagent were also added when the mixture contained potassium chlorate, potassium bromate or potassium ferricyanide. The mixture containing potassium chlorate was heated to 80° C for about ten minutes in an atmosphere of carbon dioxide and then allowed to cool. In case of potassium ferricyanide, 5 ml of freshly prepared solution of ferric chloride[2] (containing 1.0 g per 100 ml), 20 ml of 1*N* HCl, 30 ml of water and excess of ferrous ethylenediamine sulphate solution were added. The precipitate of $Fe_3[Fe(CN)_6]_2$ formed, was filtered and thoroughly washed with water. The filtrate, containing the excess of ferrous ethylenediamine sulphate, was mixed with 10 ml of Zimmermann's reagent and 30 ml of phosphoric acid mixture. In each case the excess of ferrous ethylenediamine sulphate was titrated against standard potassium permanganate solution.

All the titrations were repeated and the excess of ferrous ethylenediamine sulphate was titrated against standard potassium dichromate solution, using diphenylamine as an indicator. 30 ml phosphoric acid mixture and two drops of one per cent diphenylamine solution in concentrated sulphuric acid were used in each of the titrations with potassium dichromate. Necessary indicator correction was made in these titrations.

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* For II, see *Anal. Chim. Acta*, 11 (1954) 317.

From the amount of potassium permanganate or potassium dichromate used in each titration, except in case of potassium bromate and potassium metaperiodate, the amount of ferrous ethylenediamine sulphate required for the reduction of each substance, and consequently the amount of each substance, was determined. In the case of potassium bromate or potassium metaperiodate, the end-point was not sharp when the excess of ferrous ethylenediamine sulphate was titrated against standard potassium dichromate; while accurate volumetric observations were made with standard potassium permanganate solution. Potassium bromate and potassium metaperiodate were, therefore, estimated from the amount of potassium permanganate used in these titrations.

Phosphoric acid mixture was prepared by mixing 75 ml H_2SO_4(Sp. gr. 1.84) with 75 ml H_3PO_4 (Sp. gr. 1.75) and diluting it to 500 ml with water.

All chemicals, except ceric sulphate, used in this investigation were of guaranteed purity. Ceric sulphate was standardized with A.R. arsenious oxide[3].

The results given in Tables I to IX show that the substances can be determined indirectly by the volumetric method, using ferrous ethylenediamine sulphate (FES) as a reducing agent in acid medium.

TABLE I

POTASSIUM CHLORATE

$KClO_3$ taken g	N/20 FES added ml	N/20 $KMnO_4$ used for excess FES ml	N/20 $K_2Cr_2O_7$ used for excess FES ml	N/20 FES used by $KClO_3$ ml	$KClO_3$ found g
0.0041	25.00	21.00	21.00	4.00	0.0041
0.0071	25.00	18.00	18.00	7.00	0.0071
0.0112	25.00	13.95	13.95	11.05	0.0113
0.0153	25.00	10.00	10.00	15.00	0.0153
0.0183	25.00	6.95	6.95	18.05	0.0184

TABLE II

POTASSIUM BROMATE

$KBrO_3$ taken g	N/20 FES added ml	N/20 $KMnO_4$ used for excess FES. ml	N/20 $K_2Cr_2O_7$ used for excess FES ml	N/20 FES used by $KBrO_3$ ml	$KBrO_3$ found g
0.0056	25.00	21.00	21.40	4.00	0.0056
0.0097	25.00	18.00	18.35	7.00	0.0097
0.0153	25.00	14.00	14.30	11.00	0.0153
0.0202	25.00	10.50	10.70	14.50	0.0201
0.0260	25.00	6.30	6.45	18.70	0.0260

TABLE III

POTASSIUM METAPERIODATE

KIO_4 taken g	N/20 FES added ml	N/20 $KMnO_4$ used for excess FES ml	N/20 $K_2Cr_2O_7$ used for excess FES ml	N/20 FES used by KIO_4 ml	KIO_4 found g
0.0172	20.00	17.00	16.80	3.00	0.0172
0.0402	20.00	13.00	12.85	7.00	0.0402
0.0546	20.00	10.50	10.35	9.50	0.0546
0.0690	20.00	8.00	7.85	12.00	0.0690
0.0863	20.00	4.95	4.90	15.05	0.0865

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TABLE IV

POTASSIUM DICHROMATE

$K_2Cr_2O_7$ taken g	N/20 FES added ml	N/20 $KMnO_4$ used for excess FES ml	N/20 $K_2Cr_2O_7$ used for excess FES ml	N/20 FES used by $K_2Cr_2O_7$ ml	$K_2Cr_2O_7$ found g
0.0098	25.00	21.00	21.00	4.00	0.0098
0.0171	25.00	18.00	18.00	7.00	0.0172
0.0269	25.00	14.00	14.00	11.00	0.0270
0.0343	25.00	11.05	11.05	13.95	0.0342
0.0441	25.00	7.00	7.00	18.00	0.0441

TABLE V

POTASSIUM FERRICYANIDE

$K_3[Fe(CN)_6]$ taken g	N/20 FES added ml	N/20 $KMnO_4$ used for excess FES ml	N/20 $K_2Cr_2O_7$ used for excess FES ml	N/20 FES used by $K_3[Fe(CN)_6]$ ml	$K_3[Fe(CN)_6]$ found g
0.0768	25.00	18.00	18.00	7.00	0.0768
0.1207	25.00	14.00	14.00	11.00	0.1207
0.1374	25.00	12.50	12.50	12.50	0.1372
0.1648	25.00	10.00	10.00	15.00	0.1646
0.1800	25.00	8.60	8.60	16.40	0.1799

TABLE VI

POTASSIUM PERMANGANATE

$KMnO_4$ taken g	N/20 FES added ml	N/20 $KMnO_4$ used for excess FES ml	N/20 $K_2Cr_2O_7$ used for excess FES ml	N/20 FES used by $KMnO_4$ ml	$KMnO_4$ found g
0.0110	15.00	8.05	8.05	6.95	0.0109
0.0158	20.00	10.00	10.00	10.00	0.0158
0.0221	25.00	11.00	11.00	14.00	0.0221
0.0316	30.00	10.00	10.00	20.00	0.0316
0.0395	38.00	13.00	13.00	25.00	0.0395

TABLE VII

POTASSIUM PERSULPHATE

$K_2S_2O_8$ taken g	N/20 FES added ml	N/20 $KMnO_4$ used for excess FES ml	N/20 $K_2Cr_2O_7$ used for excess FES ml	N/20 FES used by $K_2S_2O_8$ ml	$K_2S_2O_8$ found g
0.0287	25.00	20.80	20.80	4.20	0.0284
0.0493	25.00	17.70	17.70	7.30	0.0493
0.0770	25.00	13.60	13.60	11.40	0.0770
0.1047	25.00	9.50	9.50	15.50	0.1047
0.1257	25.00	6.45	6.45	18.55	0.1254

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TABLE VIII

HYDROGEN PEROXIDE

H_2O_2 taken g	N/20 FES added ml	N/20 $KMnO_4$ used for excess FES ml	N/20 $K_2Cr_2O_7$ used for excess FES ml	N/20 FES used by H_2O_2 ml	H_2O_2 found g
0.0033	25.00	21.00	21.00	4.00	0.0033
0.0068	25.00	17.00	17.00	8.00	0.0068
0.0096	25.00	13.70	13.70	11.30	0.0096
0.0125	25.00	10.30	10.30	14.70	0.0125
0.0162	25.00	6.00	6.00	19.00	0.0162

TABLE IX

CERIC SULPHATE

$Ce(SO_4)_2$ taken g	N/20 FES added ml	N/20 $KMnO_4$ used for excess FES ml	N/20 $K_2Cr_2O_7$ used for excess FES ml	N/20 FES used by $Ce(SO_4)_2$ ml	$Ce(SO_4)_2$ found g
0.0664	25.00	21.00	21.00	4.00	0.0664
0.1328	25.00	17.00	17.00	8.00	0.1328
0.1836	25.00	13.95	13.95	11.05	0.1835
0.2326	25.00	11.00	11.00	14.00	0.2326
0.2990	25.00	7.00	7.00	18.00	0.2990

SUMMARY

Ferrous ethylenediamine sulphate has been used as a reducing agent in acid medium for the indirect volumetric estimations of potassium chlorate, potassium bromate, potassium metaperiodate, potassium dichromate, potassium ferricyanide, potassium permanganate, potassium persulphate, hydrogen peroxide and ceric sulphate. The excess of ferrous ethylenediamine sulphate added to each of the substances was titrated with standard potassium permanganate and also with standard potassium dichromate solution. In case of potassium bromate or potassium metaperiodate the end-point was not sharp in potassium dichromate titrations; while accurate volumetric observations were made with standard potassium permanganate solution.

RÉSUMÉ

Le sulfate de fer(II) éthylènediamine a été utilisé comme réducteur, en milieu acide, pour les dosages volumétriques indirects des chlorate, bromate métaperiodate, dichromate, ferricyanure. permanganate et persulfate de potassium, du peroxyde d'hydrogène et du sulfate de cérium(IV), L'excès de sulfate de fer(II) éthylènediamine, ajouté à chacun de ces composés, en milieu acide, a été titré par une solution étalon de permanganate de potassium, ou également par une solution de dichromate de potassium. Dans le cas du bromate de potassium ou du métaperiodate de potassium, le virage n'est pas net avec le dichromate de potassium, contrairement à celui obtenu avec le permanganate de potassium.

ZUSAMMENFASSUNG

Das Eisen(II) äthylendiaminsulfat wurde als reduzierende Substanz in saurem Milieu verwendet für die indirekten volumetrischen Bestimmungen von Kaliumchlorat, Kaliumbromat, Kaliummetaperiodat, Kaliumbichromat, Kaliumferricyanid, Kaliumpermanganat, Kaliumpersulfat, Wasserstoffsuperoxyd und Cerium(IV) sulfat. Der Überschuss von Eisen(II) äthylendiaminsulfat, welches zu diesen Stoffen in saurem Milieu zugegeben wurde, wurde mit einer Vergleichslösung von Kaliumpermanganat, oder ebenfalls mit einer Vergleichslösung von Kaliumbichromat titriert. Im Falle von Kaliumbromat, oder Kaliummetaperiodat ist der Umschlagspunkt mit Kaliumbichromat nicht deutlich, im Gegensatz zu dem, den man mit Kaliumpermanganat erhält.

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THE DETERMINATION OF COPPER BY COMPLEXOMETRIC TITRATION WITH ETHYLENEDIAMINETETRAACETIC ACID

by

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PŘIBIL, KOUDELA AND MATYSKA[1] have discussed the theory and some applications of redox titrations in which the titrant has no reducing or oxidizing action. In particular they considered the titration of ferric iron with ethylenediaminetetraacetic acid (EDTA). This titration depends on the change brought about in the redox potential of the ferric-ferrous system when the iron is complexed with EDTA. These workers also mentioned that the cuprous-cupric system might also fulfil the necessary conditions for such a titration, but apparently they did not pursue the matter any further.

In previous work[2] on the interaction of copper with EDTA we have noted the marked stabilizing effect of EDTA on copper (II), thus increasing the reducing power of copper (I), which may be compared with the behaviour of iron under similar conditions[2]. We have now examined the copper (II) - copper (I) - EDTA system to find if a complexometric titration can also be effected in this case.

0.1*N* solutions of cupric ammonium chloride were titrated with 0.1*N* solutions of EDTA, the course of the titrations being followed potentiometrically using bright platinum and saturated calomel electrodes and a direct reading pH-meter/potentiometer.

At pH 3 (the pH resulting from the addition of EDTA (disodium salt) to a neutral solution of cupric ammonium chloride), the end-point was quite sharp, but the potential began to change with increasing rapidity before the end-point was reached. In solutions buffered at pH 6 by the addition of ammonium acetate, there was very little change in potential until much nearer equivalence. Accordingly, a greater change in potential resulted at the end-point thus making its location much more precise.

Titrations were also effected at pH 1 and pH 10. At pH 1 there was only a gradual change in potential since complex formation did not take place in strongly acid solution. At pH 10 (the pH being adjusted by the addition of ammonia solution), the potential change at the end-point was very small because the cupric ion was being transformed from one stabilized state to another, and the stabilities of the two complexes were such that the change in potential in going from the ammonia complex to the EDTA one was only small. Titrations were therefore best effected in the presence of ammonium acetate.

The concentration range was then extended by titration of 0.01, 0.04, 0.2 and 0.5*N* cupric solutions with solutions of EDTA of comparable strengths. The end-points obtained with the strong solutions were, as expected, extremely sharp; and even those obtained with the more dilute solutions were still satisfactory, although with the 0.01N solutions it was preferable to plot a graph of dE/dV against V (*i.e.*, the rate of change of potential with the volume of titrant added) in order to locate the end-point more precisely.

Typical titration curves are shown in Figs. 1 and 2, and results in Table 1.

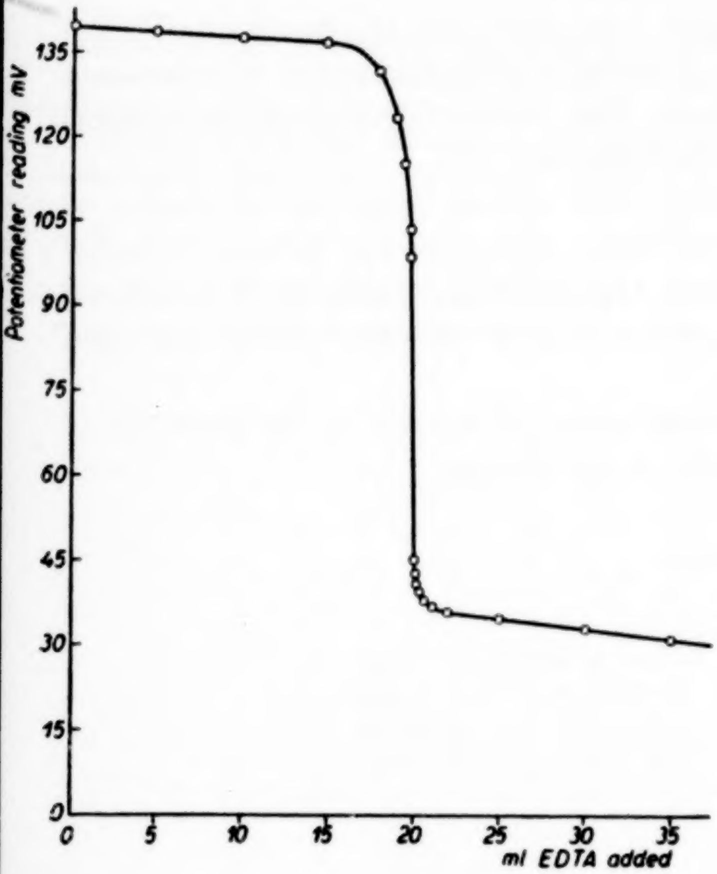

Fig. 1

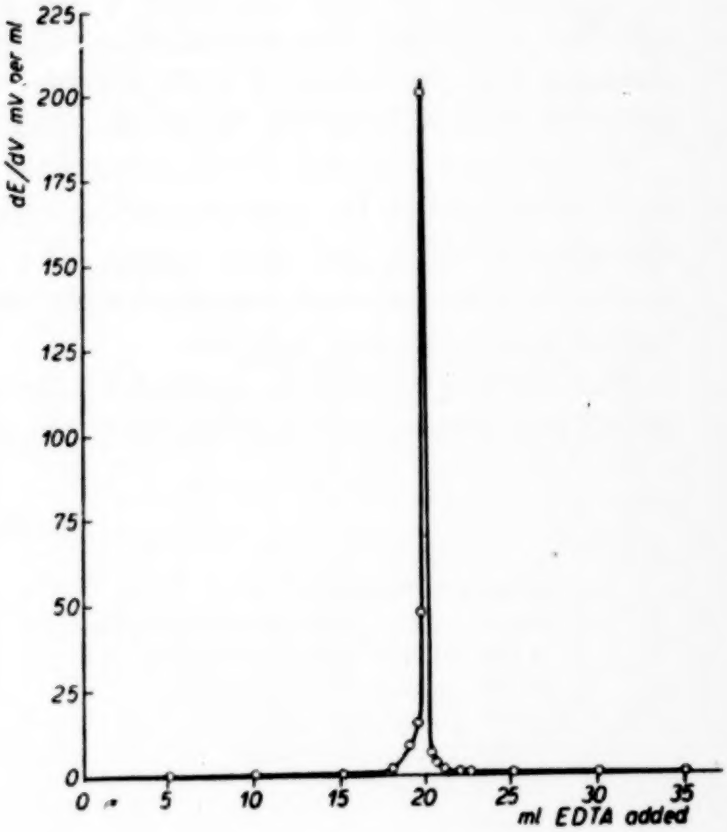

Fig. 2

TABLE I

ml 0.5N cupric taken	20.00	20.00	50.00	50.00	10.00	10.00
ml 0.5N EDTA required	20.00	20.02	50.00	50.00	10.00	9.98
ml 0.2N cupric taken	20.00	20.00	50.00	50.00	10.00	10.00
ml 0.2N EDTA required	20,02	20.00	50.00	50.02	10.02	9.98
ml 0.1N cupric taken	20.00	20.00	50.00	50.00	10.00	10.00
ml 0.1N EDTA required	20.02	19.98	50.02	49.98	10.00	9.96
ml 0.04N cupric taken	20.00	20.00	50.00	50.00	10.00	10.00
ml 0.04N EDTA required	20.02	19.96	50.00	50.04	10.04	9.98
ml 0.01N cupric taken	20.00	20.00	50.00	50.00	10.00	10.00
ml 0.01N EDTA required	20.00	19.96	50.02	50.00	9.94	10.02

The interfering effect of a selected number of ions was next examined, these being ferric iron, aluminium, cadmium, zinc, manganese, nickel, cobalt, and lead.

The stability of the ferric-EDTA complex is greater than that of the corresponding copper complex and the two potential ranges are fairly well separated. It was expected therefore that the two ions could be titrated in the presence of each other, and that a titration curve with a double step would result. Such a curve was in fact obtained, but although the second step corresponding to the copper was almost as sharp as the normal copper end-point, the step corresponding to the iron had a very gentle inflection, making it impossible to determine the iron and therefore the copper. This effect was due presumably to the stabilities of the two complexes being too close together for the whole of the iron to be complexed before the copper.

An attempt was made to suppress the complex formation with the ferric iron by the addition of citrate, for according to Přibil, Koudela and Matyska[1] this forms a stronger complex than EDTA with ferric iron. The citrate complexed the copper, however, thus making the cupric end-point also indistinct.

The stabilities of the EDTA complexes of the other metals listed are all similar to each other, and to the stability of the copper complex, moreover the various potential changes are all in the same region. This meant that all the metals listed interfered in the determination of copper, for the end-point obtained corresponded to the total complexable metal in solution.

The method cannot be applied to the determination of copper in the presence of interfering metals and a preliminary separation, is necessary.

EXPERIMENTAL

Reagents required: —

0.1N cupric ammonium chloride	27.75 g in 1 l of water
0.1N EDTA (disodium salt)	37.23 g in 1 l of water
0.1N sodium thiosulphate	24.82 g in 1 l of water
0.1N potassium iodate	3.567 g in 1 l of water
10% potassium iodide	
2N sulphuric acid	
starch	
ammonium acetate (solid).	

The cupric ammonium chloride solution was standardized by addition of an acidified solution of potassium iodide, followed by titration of the liberated iodine with sodium thiosulphate using starch as indicator. The sodium thiosulphate solution was previously standardized by titration against standard potassium iodate in a similar manner.

20 ml of the cupric ammonium chloride solution were placed in a 250 ml beaker and buffered by the addition of 3-5 g of solid ammonium acetate. The mixture was then titrated potentiometrically with the EDTA solution using bright platinum and saturated calomel electrodes. The solution was stirred continuously throughout the titration by means of a magnetic stirrer.

A preliminary rough titration was carried out in order to find the end-point to within 0.5 ml. An accurate titration was then effected as described, the EDTA solution being added rapidly at first, more slowly as the end-point was approached, and dropwise, with a one-minute pause after each addition, over the last 0.5 ml of reagent.

ACKNOWLEDGEMENTS

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SUMMARY

A method has been developed for the determination of cupric copper by complexometric titration with ethylenediaminetetraacetic acid. The titrations were followed potentiometrically, and were effected at pH 5-6 in the presence of an ammonium acetate buffer. Interfering metals such as ferric iron, aluminium, cadmium, zinc, manganese, nickel, cobalt and lead must be removed by a preliminary separation.

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RÉSUMÉ

Une méthode est proposée pour le dosage du cuivre(II) par titration complexométrique au moyen d'acide éthylènediaminotétraacétique. Cette titration est effectuée par potentiométrie, au pH 5-6, en présence d'un tampon à l'acétate d'ammonium. Des cations gênants, tels que le fer(III), l'aluminium, le cadmium, le zinc, le manganèse, le nickel, le cobalt et le plomb doivent être éliminés par une séparation préalable.

ZUSAMMENFASSUNG

Es wird eine Methode vorgeschlagen, Kupfer(II) mit einer komplexometrischen Titration zu bestimmen mit Hilfe der Äthylendiamintetraessigsäure. Diese Titration wird potentiometrisch ausgeführt bei pH 5-6, in Anwesenheit eines Ammoniumacetatpuffers. Die störenden Kationen, wie Eisen(III), Aluminium, Kadmium, Zink, Mangan, Nickel, Kobalt und Blei müssen durch eine vorausgehende Abtrennung eliminiert werden.

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THE DETERMINATION OF ZIRCONIUM IN ITS BINARY ALLOYS WITH NIOBIUM AND TANTALUM

by

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INTRODUCTION

In preliminary considerations of possible procedures for the determination of zirconium in the presence of niobium or tantalum, it was difficult to reach any definite conclusions because of the general lack of information in the literature. For example, workers reporting on the various new organic reagents for zirconium (*e.g.* phthalic[1] and tetrachlorophthalic acids[2], *m*-cresoxyacetic acid[3], mandelic acid[4] and various substituted derivatives[5]) have generally avoided any mention of the behaviour of niobium or tantalum under the optimum solution conditions for the precipitation of zirconium. In many cases the zirconium precipitation is carried out from weakly acidic solutions from which hydrolysis of niobium or tantalum takes place, preventing a clean separation of zirconium from these elements. Further difficulty could also be anticipated from the need to use hydrofluoric acid in dissolving metallic zirconium, niobium or tantalum. The removal of fluoride ions from a solution by evaporation to fumes of perchloric acid would not serve in this case since the earth acid elements are dehydrated. The only available procedure for satisfactorily freeing the solution from hydrofluoric acid involved evaporation to fumes of sulphuric acid. Unfortunately these solution conditions are unsuitable for the application of the newer organic reagents because of the general inhibiting effect of sulphate ions in such precipitations. In the case of a reagent such as cupferron which can be used in a sulphate medium for the precipitation of zirconium, the simultaneous precipitation of niobium and tantalum prevents any useful separation of these elements.

EXPERIMENTAL

Milner and Phennah[6] recently reported a volumetric procedure for the determination of zirconium by EDTA and preliminary experiments were directed to the study of the behaviour of niobium and tantalum under the titration conditions. At the pH necessary for the titrations, however, hydrolysis of the earth acid elements took place and the precipitate tended to mask the end-point. In further experiments, the retention of niobium and tantalum in solution was accomplished by the addition of complexing agents such as lactic, citric and maleic acids. No improvement in the zirconium determination resulted because these complexing agents also complexed the free ferric ions present after the completion of the back titration and poor end-points were obtained.

Hydrogen peroxide is reported as forming soluble complexes with tantalum[7] and niobium[8] in acid solutions and some attention was, therefore, given to the use of this reagent for retaining the earth acid elements in solution. Under the titration conditions there was no precipitation of either niobium or tantalum in the presence of hydrogen peroxide and the end-point of the iron back titration could be readily detected. However, high values for the recovery of zirconium were obtained, especially in the presence of niobium. These results suggested the existence of a complex between niobium and EDTA, which has since been confirmed polarographically by FERRETT AND MILNER[9]. In further experiments with niobium alone, no quantitative relationship could be found between the amount of EDTA consumed and the amount of niobium in solution. It was concluded, therefore, that the niobium-EDTA complex is very weak and the addition of ferric iron in the back titration causes the breakdown of the niobium complex in favour of the strong iron-EDTA complex.

Some preliminary separation of the niobium or tantalum was clearly necessary before the EDTA titration technique could be applied to the determination of zirconium in solutions with large Nb/Zr or Ta/Zr ratios. Simultaneously with this investigation, MILNER, BARNETT AND SMALES[10] were studying the solvent extraction of niobium and tantalum into methyl *iso*butyl ketone (hexone) from acid fluoride solutions. It was shown that large amounts of niobium or tantalum can be separated from zirconium by extracting a solution $10M$ in hydrofluoric acid, $6M$ in sulphuric acid and $2.2M$ in ammonium fluoride with hexone. In the present problem, the omission from the aqueous solution of ammonium fluoride, which was originally included to assist phase separation, was considered advisable because of difficulties in removal before the determination of zirconium. From solutions $10M$ in hydrofluoric acid and $6M$ in sulphuric acid extraction coefficients for tantalum, niobium and zirconium were found to be > 250, 67 and $2.5 \cdot 10^{-2}$ respectively. It was concluded from these values that only a single solvent extraction could be carried out without risk of some loss of zirconium. A single extraction would be sufficient to remove the bulk of the Nb or Ta, but with solutions containing high Nb/Zr or Ta/Zr ratios, there would be small amounts of niobium or tantalum unextracted. To remove these residual amounts of the earth acid elements a further separation by a different technique would be necessary. A suitable purification of the zirconium was found to be accomplished by the precipitation of zirconium hydroxide with ammonia in the presence of hydrogen peroxide and details of the complete procedure for this determination are as follows:

Procedure for the determination of zirconium in its binary alloys with tantalum or niobium

Special apparatus

Polythene separating funnels. Saw off the bottom of a 250 ml or 500 ml polythene bottle and fuse on to it a suitable polythene funnel. This is best done with a hot air gun. Cut off the stem of the funnel, leaving about ½in. and fit over it a piece of polythene or P.V.C. tubing making sure it is a tight fit. Close the tubing with a screw clip.

Reagents

Equilibrated hexone. Shake 300 ml of hexone (methyl *iso*butyl ketone) for 10 min with 100 ml of a solution $10M$ in HF and $6M$ in H_2SO_4. Use a 500 ml polythene separating funnel. Allow the layers to separate and run off the lower aqueous layer. Discard. Store the conditioned hexone in a polythene bottle. This reagent remains satisfactory for no more than one week.

Wash solution. Add 435 ml of 40% HF very slowly to 334 ml of concentrated H_2SO_4 (s.g. 1.84) in a polythene beaker standing in a cold water bath, stirring constantly. Dilute the solution to 1 litre and store in a polythene bottle.

0.100*M iron solution.* Dissolve 5.585 g "Specpure" iron in 20 ml of hot hydrochloric acid (s.g. 1.16). Dilute the solution with water and oxidize the iron with nitric acid (s.g. 1.42). Dilute to 1 litre with water in a volumetric flask. This solution may be diluted suitably when determining small amounts of zirconium.

0.001*M EDTA solution.* Dissolve 37.23 g of disodium ethylenediaminetetraacetic acid in water and dilute to 1 litre.

Standardize the solution by taking 25 ml aliquots, add 3 g of ammonium acetate, dilute to 150-200 ml with water, add 0.2 g of salicylic acid and titrate with the standard iron solution to the first permanent brown colour.

Procedure

Take a weight of sample to contain from 5 to 100 mg of zirconium. Dissolve alloys by covering the accurately weighed sample with 20 ml of 1:1 v/v nitric acid, warming slightly and adding 40% hydrofluoric acid dropwise. To the solution in a platinum dish, add 15 ml of 1:1 v/v sulphuric acid and evaporate until heavy fumes are evolved (*Note* 1). Cool the solution and add 10 ml of 40% hydrofluoric acid, swirl the dish to mix the contents and transfer to a polythene separating funnel. Wash the dish with 7.5 ml of 10% v/v sulphuric acid solution and transfer the washings to the funnel. To the solution in the funnel, add 25 ml of conditioned hexone and shake for 5 min. Allow the phases to separate, run off the lower aqueous layer into the original platinum dish, wash the hexone in the funnel with 10 ml of wash solution and add the washings to the solution in the dish. Evaporate the solution nearly to fumes, add nitric acid dropwise to oxidize organic matter, then continue evaporating until fumes of sulphuric acid appear and fume strongly for 10 minutes. Cool the solution and dilute cautiously with water. Transfer to a 250 ml centrifuge tube and dilute to 100 ml with water. Stand the centrifuge tube in an ice bath and add ammonia (sp. gr. 0.88) slowly with stirring until the solution is alkaline to litmus (*Note* 2). Add 5 ml of 100 volume hydrogen peroxide and stir for 5 minutes. Centrifuge for 5 min at 1500 r.p.m. Decant the supernate through a Whatman No. 40 filter paper. Wash the precipitate with 2% ammonium chloride solution, centrifuge and decant the supernate through the filter paper. Pour 20 ml of hot 1:1 v/v hydrochloric acid into the centrifuge tube, swirl to dissolve the precipitate and transfer to a 400 ml beaker. Open out the filter paper over the beaker and wash it with a stream of hot 20% hydrochloric acid, catching the washings in the beaker. Cover the beaker with a clock glass and boil the solution vigorously for 10 minutes. Cool and add an excess of standard EDTA solution, add 3 g of ammonium acetate and adjust the pH to 5-6. Boil the solution for 2 minutes, cool to room temperature, add 0.2 g of salicylic acid and titrate with standard iron solution to the first permanent brown colour.

Note 1. During the evaporation some tantalum may come out of solution and great care must be exercised to avoid losses by spattering.

Note 2. For systems containing tantalum allow the temperature to rise to about 30° C before adding hydrogen peroxide.

The study of the separation of zirconium from niobium or tantalum by the ammonia-hydrogen peroxide procedure

During the investigations on the behaviour of niobium and tantalum with EDTA in the presence of hydrogen peroxide, it was found that neither of these elements was precipitated by ammonia from solutions containing hydrogen peroxide. Zirconium, however, was quantitatively precipitated under the same conditions. This behaviour was, therefore, studied in some detail with the object of evaluating its potentialities for separating zirconium from niobium or tantalum. Synthetic solutions were prepared by dissolving suitable weights of niobium or tantalum metal in a mixture of nitric and hydrofluoric acids, adding an aliquot of a standard zirconium solution and then evaporating to fumes with sulphuric acid. These solutions were then transferred to a centrifuge tube and the ammonia-hydrogen peroxide treatment carried out as described previously in the latter part of the complete procedure. In all the cases quoted in the results, a second ammonia-hydrogen peroxide treatment was performed before the EDTA titration was applied because at the higher ratios of Nb/Zr or Ta/Zr the separations were visibly incomplete. In addition, the temperature of solutions in experiments with tantalum was allowed to rise to about 30° C because the hydrous tantalic acid proved more difficult to redissolve in hydrogen peroxide than did the hydrous niobic acid. Recovery results for amounts of zirconium at the 15 mg level are given in Table I and it will be observed that it is possible to separate zirconium from twenty times its own weight of niobium, or three times its own weight of tantalum.

TABLE I

RESULTS FOR THE SEPARATION OF ZIRCONIUM FROM NIOBIUM AND TANTALUM BY A DOUBLE AMMONIA-HYDROGEN PEROXIDE PRECIPITATION

Zr taken (mg)	*Ta or Nb taken (mg)*	*Ratio Nb/Zr or Ta/Zr*	*Wt Zr found (mg)*	*Recovery %*
14.82	15 mg Nb	1/1	14.89	100.5
	50 ,, ,,	3.3/1	14.86	100.3
	100 ,, ,,	6.7/1	14.73	99.4
	150 ,, ,,	10/1	14.84	100.1
	300 ,, ,,	20/1	14.59	98.5
	500 ,, ,,	33/1	14.22	95.6
15.33	15 ,, Ta	1/1	15.12	98.6
15.33	50 ,, ,,	3.3/1	15.11	98.6
15.33	200 ,, ,,	13.3/1	14.38	93.8

Results for the separation of zirconium from niobium or tantalum by the complete procedure

This procedure was applied to synthetic alloy solutions prepared by dissolving suitable amounts of zirconium and niobium or tantalum metals in a mixture of nitric and hydrofluoric acids as described. After the addition of 15 ml of (1 + 1) sulphuric acid, the solution was evaporated to fumes to remove the solvent acids, great care being taken with zirconium-tantalum solutions as tantalum came out of solution when present in amounts greater than 200 mg. The solution was cooled and 10 ml of 40% hydrofluoric acid added, when any tantalum out of solution redissolved. After the extraction with hexone, a single ammonia-hydrogen peroxide treatment proved sufficient in this work since with niobium, even a 100/1 excess of niobium over zirconium was reduced to roughly equal proportions by the hexone extraction. With tantalum and zirconium solutions an even greater reduction of the Ta/Zr ratio was achieved due to the higher extraction coefficient. Results obtained for the analysis of synthetic alloy solutions are given in Table II.

TABLE II

RESULTS FOR THE SEPARATION OF ZIRCONIUM FROM NIOBIUM BY THE COMPLETE PROCEDURE

Zr taken (mg)	*Nb taken (mg)*	*Ratio Nb/Zr*	*Zr found (mg)*	*Recovery %*
4.95	nil	—	4.93	99.6
4.95	250	50/1	5.20	105
4.95	500	100/1	5.08	102.6
14.62	nil	—	14.53	99.4
14.62	500	33/1	14.78	101.1
13.48	1000	72/1	13.84	102.7
48.2	nil	—	48.0	99.6
48.2	100	2/1	48.1	99.8
48.2	250	5/1	48.1	99.8
48.2	500	10/1	48.8	101.2
99.0	nil	—	98.8	99.8
99.0	100	1/1	98.8	99.8
99.0	500	5/1	98.7	99.7

Zr teken (mg)	*Ta taken (mg)*	*Ratio Ta/Zr*	*Zr found (mg)*	*Recovery %*
4.97	500	100/1	4.96	100.2
20.40	50	2.5/1	20.45	100.2
20.40	100	5/1	20.38	100.0
20.40	250	12/1	20.45	100.2
20.60	500	24/1	20.50	99.5
40.6	100	2.5/1	40.8	100.5
48.4	250	5/1	48.2	99.6
48.4	500	10/1	48.4	100.0
96.5	100	1/1	96.5	100.0
96.5	500	5/1	96.6	100.1

All results are the mean of duplicate experiments.

SUMMARY

A procedure is presented for the determination of zirconium in the presence of niobium or tantalum. The bulk of the niobium or tantalum is first removed by extracting with hexone from a 10*M* hydrofluoric acid, 6*M* sulphuric acid solution of the sample. The zirconium is then separated from any unextracted earth acid element by precipitation with ammonium hydroxide followed by the addition of hydrogen peroxide. Under these conditions, both the niobium and tantalum form soluble peroxy complexes whereas the zirconium is completely precipitated from solution. After the separation of the precipitate by filtration, it is re-dissolved in hydrochloric acid and the zirconium concentration is finally determined by titration with ethylenediaminetetraacetic acid.

RÉSUMÉ

Une méthode est proposée pour le dosage du zirconium en présence de niobium et de tantale. Le niobium et le tantale sont préalablement éliminés, en grande partie par extraction dans l'hexone, de solutions 10*M* en acide fluorhydrique et 6*M* en acide sulfurique; ensuite, le zirconium est séparé des éléments non extraits par précipitation au moyen d'hydroxyde d'ammonium, suivie d'une addition de peroxyde d'hydrogène. Dans ces conditions, soit le niobium, soit le tantale forment des peroxycomplexes solubles, tandis que le zirconium précipite complètement. Après filtration, le précipité est redissous dans l'acide chlorhydrique, la concentration en zirconium est finalement déterminée par titration au moyen de l'acide éthylènediaminetétraacétique.

ZUSAMMENFASSUNG

Es wird eine Methode vorgeschlagen, um Zirkonium in Gegenwart von Niobium und Tantal zu bestimmen. Das Niobium und das Tantal werden vorher zum grossen Teil eliminiert durch eine Extraktion mit Hexon, aus einer 10*M* Fluorwasserstoff- und 6*M* Schwefelsäure-Lösung. Darauf wird das Zirkonium von den Elementen, welche nicht ausgezogen wurden, getrennt durch eine Ausfällung mittels Ammoniumhydroxyd, welcher eine Zugabe von Wasserstoffperoxyd folgt. Unter diesen Bedingungen bilden das Niobium und das Tantal lösliche Peroxy-Komplexe, während das Zirkonium vollständig ausfällt. Nach der Filtration wird der Niederschlag in Salzsäure aufgelöst. Die Zirkonium-Konzentration wird schlussendlich durch eine Titration mit Äthylendiamintetraessigsäure bestimmt.

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DETERMINATION OF ALUMINIUM IN PLAIN STEEL USING EDTA AND DICHLORODIETHYL ETHER

by

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INTRODUCTION

There are a number of difficulties peculiar to the analysis of steel which have to be faced in developing any method of analysing this metal. For instance, the large quantities of iron present have usually to be separated from the impurities which are being analysed. These difficulties are manifested in physical methods by the necessity of a large spectrograph in spectrographic analysis and the difficulty in eliminating the iron step in polarographic analysis. In wet methods the separation of the iron is often difficult and this is particularly so in the estimation of aluminium in steel where the properties of the elements being separated are very similar. The principal methods used for this have included the mercury cathode separation, organic solvent extraction processes *etc.*, but the procedures have proved either lengthy or incomplete. Among the extraction processes we find ether, dichlorodiethyl ether, amyl acetate[1] and ether with a tetrahydro furan[2]. In the present work, attention was paid to the use of dichlorodiethyl ether (dichloroether) and amyl acetate.

SEPARATION OF IRON FROM ALUMINIUM

Amyl acetate was first tried as an extraction solvent for the iron. Under the conditions recommended the extraction was found to be rapid and satisfactory leaving a bright green solution. The main disadvantages of amyl acetate were that it was a relatively expensive reagent, moreover it was somewhat soluble in the strongly acid solution and it was found very difficult to carry out blank determinations.

Attemps to use dichloroether were at first unsatisfactory but later good results were obtained when the commercial product was steam distilled, the first and last fractions being discarded. The first fraction in particular was often coloured, but the middle fraction was quite colourless, especially after drying. This reagent was preferred to amyl acetate because: —

1. The layer was heavier than water and therefore more easily separated off.
2. It was not such a fire hazard.
3. It was easily recoverable by washing with acidified water (as was the amyl acetate).
4. It was not so soluble in the strongly acid solution as amyl acetate.
5. It was a cheap reagent in ready supply. However it was not so rapid in extracting the iron as the amyl acetate and usually required an extra extraction.

After extraction of the iron, the remaining strongly acid solution was bright green in colour. This has been said to be due to the presence of photochemically reduced iron[1]. However, on dilution the colour rapidly faded, also it was not found possible to oxidize this reduced iron. The colour was later found to be due to the presence of small quantities of copper, nickel and manganese from the original steel sample.

Having extracted the iron, it was decided to develop gravimetric, volumetric and colorimetric methods for determining the aluminium.

GRAVIMETRIC METHOD

The basis of the method was that when the bulk of the iron had been removed, the aluminium could be separated from many interfering elements (copper, nickel, manganese, cobalt *etc.*) by precipitating with ammonia-ammonium chloride solution. After filtering the precipitate was redissolved in acid, and EDTA was added; this complexed the metals present. The solution was then made alkaline with potassium hydroxide and the precipitate, containing the last traces of iron, filtered off. The pH of the solution was adjusted to neutral and oxine added which precipitated the aluminium. This was filtered off on a sintered glass crucible and weighed.

It was found that if the precipitate was filtered while the solution was still caustic that the crucible lost weight and the results were unreliable. Interference from silicon was eliminated by adding a little hydrofluoric acid to the mineral acid used to dissolve the sample. The use of potassium fluoride caused the precipitation of potassium silico fluoride which must be eliminated, hence it is advisable to keep to the acid. It is advisable to maintain a reasonable bulk of solution (50-100 ml) before precipitation with ammonia-ammonium chloride solution, to avoid interference by hydrated manganese dioxide which may otherwise precipitate. Any which does come through may be eliminated by adding H_2O_2 with the EDTA/potassium hydroxide precipitation of iron, when manganese is precipitated as MnO_2 and can be filtered off with the iron.

Since standard steels were not available samples were provided by making up a stock solution of a killed mild steel. Aliquots were taken and known varying amounts of aluminium were added. The results obtained are given in Table I.

TABLE I

ALUMINIUM IN STEEL. GRAVIMETRIC METHOD

mg Al in plain steel (5 g sample)	*Al added (mg)*	*Total Al (mg)*	*Al found (mg)*
0.1	Nil	0.1	0.1
0.1	,,	0.1	0.2
0.1	,,	0.1	0.1
0.1	0.5	0.6	0.6
0.1	0.5	0.6	0.5
0.1	0.5	0.6	0.6
0.1	2.8	2.9	2.7
0.1	2.8	2.9	2.5
0.1	2.8	2.9	2.9
0.1	5.0	5.1	5.0
0.1	5.0	5.1	4.7
0.1	5.0	5.1	4.8
0.1	29.8	29.9	29.7
0.1	29.8	29.9	29.4
0.1	29.8	29.9	29.4

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RECOMMENDED METHOD

Reagents

ββ'Dichlorodiethyl ether	Technical reagent, purified by steam distillation as previously described.
Disodium EDTA	0.2*M* solution in water.
Oxine solution	1 g oxine (8-hydroxy-quinoline) dissolved in 2*N* acetic acid (total vol 50 ml). This is added slowly to 50% (v/v) ammonia warmed to 70° C. Rapid addition leads to precipitation of the reagent which only redissolves with difficulty.
Hydrochloric acid	Concentrated AnalaR reagent.
Nitric acid	Concentrated AnalaR reagent.
Hydrofluoric acid	40% w/w hydrofluoric acid/water.
Ammonia	50% v/v 0.880 s.g. ammonia/water.
Ammonium chloride	1% w/v ammonium chloride in water.
Potassium chloride	1% w/v potassium chloride in water.
Acetic acid solution	30% glacial acetic acid in water.
Hydrogen peroxide	100 vol H_2O_2

Procedure

Dissolve 5 g of steel in hydrochloric acid and oxidize with nitric acid. Add a few ml of hydrofluoric acid to remove silica. Evaporate until a paste just begins to form, cool and make up to 50, ml in conc. hydrochloric acid, making a solution about 9*N* HCl. Transfer to a separating funnel washing out with conc. HCl and shake with 100 ml of dichloroether. Discard the lower iron-containing layer, repeat the extraction with two further 50 ml portions of dichloroether.

Transfer the remaining solution to a 125 ml beaker and evaporate to dryness without baking, dissolve in hydrochloric acid (1 ml of 5*N* solution) and dilute to 10 ml. Filter off silica if necessary, washing with 5% hydrochloric acid. Adjust the volume of solution to 50 ml, add solid ammonium chloride (2-3 g), boil and add sufficient ammonium hydroxide to precipitate aluminium, *etc.* Boil for a further 5 minutes. Filter and wash with ammonium chloride solution. Redissolve in hydrochloric acid and boil off excess acid. Adjust the volume to about 10 ml, add disodium EDTA (5 ml) followed by potassium hydroxide (2*N*) until the solution is about pH 11 (shown by using universal indicator). Boil and add a few drops of hydrogen peroxide to precipitate any manganese which may have come through. Cool the solution slowly and filter off the iron and manganese. Wash with potassium chloride and discard the precipitate. Neutralize the filtrate and evaporate to about 20 ml. Cool to about 60° C and add oxine until the solution is yellow and neutralize with dilute acetic acid.

Allow the precipitate to stand for 10 minutes at 60° C — higher temperature should be avoided particularly for small quantities of aluminium. Filter through a weighed No. 4 sintered glass crucible, wash the precipitate with hot water and dry at 102-220° C[3] and weigh as $Al(C_9H_6ON)_3$.

Weight of precipitate X 00.5871 = wt of aluminium. If the aluminium is expected to be less than 0.05%, only 0.5 ml of disodium EDTA should be used and volume of the filtrate adjusted to 5 ml before the addition of oxine. Excessive use of reagents should also be avoided, otherwise crystallization may occur in the low bulk.

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SUMMARY

A gravimetric method for determining aluminium in steel has been developed. This involves the separation of iron using steam-distilled dichlorodiethylether and the precipitation of aluminium from the disodium salt of EDTA.

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RÉSUMÉ

Une méthode gravimétrique est proposée pour le dosage de l'aluminium dans les aciers. Elle est basée sur la séparation du fer par distillation au moyen de l'éther dichlorodiéthylique et sur la précipitation de l'aluminium au moyen du sel disodique de l'acide éthylènediaminotétraacétique.

ZUSAMMENFASSUNG

Es wird eine gravimetrische Methode vorgeschlagen, um Aluminium in Stahl zu bestimmen. Sie beruht auf der Abtrennung des Eisens mittels einer Destillation mit Dichlorodiäthyläther und auf der Ausfällung des Aluminiums mit dem Dinatriumsalz der Äthylendiaminotetraessigsäure.

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THE EXTRACTION OF SOME METALLIC BROMIDES FROM AQUEOUS SOLUTIONS WITH METHYL ETHYL KETONE AND METHYL *ISO*-BUTYL KETONE

by

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INTRODUCTION

The technique of solvent extraction has of recent years been applied to the field of inorganic chemistry with encouraging results. It has been found possible to extract metallic salts into organic solvents in the form of a solvated association complex of the metal salt with the acid containing the same anion. A considerable amount of work has been done on metallic halides, nitrates and thiocyanates on these lines[1], but most of the work concerning the halides seems to have been restricted to chlorides. Exact information on bromides occurs only sporadically in the literature, but such as is at present available suggests that the differences observed between bromides and chlorides may be marked and analytically useful. BOCK[2] has recently conducted a systematic investigation into the extraction of metallic bromides in an attempt to remedy this situation. He has, in common with most workers in this field, chosen ether as a solvent. Isolated cases do occur in the literature in which other solvents have been used in extraction and separation studies but it is only feasible as yet to make comparisons between systems involving the use of ether as an extractant. Consequently systematic investigations with other solvents seem to be highly desirable.

An investigation of the solvent extraction of some metallic bromides has been conducted using methyl ethyl ketone (MEK) and methyl *iso*-butyl ketone (MIBK) as solvents. The metal bromides were extracted from aqueous solutions containing hydrobromic acid and/or ammonium bromide. In most of the distribution experiments two concentrations of the metal salts were investigated, *viz.* 0.1M and 0.2M. As may be expected the MIBK proved to be the more important solvent, the MEK being strictly limited in scope by its solubility in acidic aqueous solutions.

In the above way a comparison was made, not only of the behaviour of the various metals, but also of the properties of ether and MIBK as solvents in this type of work.

EXPERIMENTAL

Materials

Hydrobromic acid was a sample of the concentrated acid which by analysis was shown to have a satisfactory ratio of hydrogen: bromine.

Ammonium bromide was AnalaR grade material from which standardized solutions were prepared.

Zinc bromide was prepared from AnalaR zinc oxide and hydrobromic acid.

Cobalt bromide was the B.D.H. product.

Ferrous bromide was the B.D.H. product, solutions of which were made 0.76*M* with respect to hydrobromic acid.

Ferric bromide solutions were prepared by oxidizing ferrous bromide solutions with AnalaR bromine. Some slight excess of bromine was left in the solution for reasons which will be explained at the appropriate stage.

Nickel bromide was prepared by precipitating nickel hydroxide from nickel sulphate solution and dissolving the precipitate, freed from impurities by washing by decantation, in hydrobromic acid.

Aluminium chloride was B. P. C. grade material.

Manganese bromide was ordinary commercial grade material.

Cupric bromide was "Kahlbaum" crystalline material.

Cuprous bromide was prepared by reducing a solution of cupric bromide with sulphur dioxide. The solutions were stored under carbon dioxide.

Stannous chloride was ordinary commercial grade material. The solutions were made 5.43*M* with respect to hydrobromic acid and stored under carbon dioxide.

Stannic chlorobromide solutions were prepared by oxidizing solutions of stannous chloride with AnalaR bromine. The solutions were made 5.43*M* with respect to hydrobromic acid.

In the experiments with aluminium and tin the chlorides were used as the starting points due to the difficulties involved in the preparation of the bromides.

Specimens of bromides having a satisfactory ratio of metal: bromine were the only ones used in this work.

Apparatus

All experiments were carried out at 20° C in pyrex shaking tubes made from B 24 Quickfit ground-glass cone and socket joints.

Procedure

25 ml portions of the required aqueous mixtures were made up by placing the calculated aliquots of stock solutions in the tubes and making up to 25 ml with water. 25 ml of the appropriate ketone were then run in and the tubes stoppered and fastened. In the experiments with cuprous bromide and stannous chloride the above operations were carried out in an atmosphere of carbon dioxide.

The tubes containing the solutions were placed in the thermostat and allowed to stand for a short time to come to the correct temperature. Having attained thermal equilibrium the contents of the tubes were mixed by rotation in the thermostat for five minutes.

After this mixing, the tubes were removed from the thermostat, the contents transferred to a 50 ml burette, suitable time being allowed for drainage, and the volumes of the phases were noted.

In all cases the concentrations of the additives in the aqueous solutions were calculated on the assumption that only normal bromides were present, the formation of association complexes being neglected. It must be remembered however, that all the acid in the initial aqueous solutions may not be available for complex acid formation in the event of extraction as some of it will undoubtedly be consumed by the formation of a loose salt with the ketone.

Methods of analysis

Zinc, cobalt and aluminium were determined gravimetrically with oxine.

Nickel was determined gravimetrically with dimethylglyoxime.

Iron was precipitated as hydroxide (oxidation occurring here in the case of Fe(II)), washed free from bromide, dissolved in hydrochloric acid, reduced with stannous chloride and finally titrated with standard potassium dichromate.

Manganese was determined by the method of LINGANE AND KARPLUS[3].

Copper was first precipitated as the metal by boiling the solutions with aluminium foil. This precipitate was washed, dissolved in nitric acid and determined with iodine and sodium thiosulphate. In the case of Cu(I) the copper was first oxidized with hydrogen peroxide.

Tin was determined with standard iodine solution in an atmosphere of carbon dioxide. Sn(IV) was first reduced to Sn(II) with antimony powder and hydrochloric acid in an atmosphere of carbon dioxide.

RESULTS

Results are expressed as percentage extraction T given by:

$$T = \frac{100.E\,\dfrac{V_o}{V_w}}{E\,\dfrac{V_o}{V_w} + 1}$$

where E is the extraction coefficient $\frac{C_o}{C_w}$ and

C_o is the concentration of metal in the organic phase,
C_w is the concentration of metal in the aqueous phase,
V_o is the volume of the organic phase and
V_w is the volume of the aqueous phase after distribution.
It may be noted here that the ratio of the volumes of the phases was extremely close to unity in all the work with MIBK.

In all the illustrations which follow, the percentage extraction T is plotted against the variant in the initial aqueous solution. As the partition isotherms of the metals investigated at two concentrations were very nearly linear over this particular range, especially in the case of MIBK, the results for the higher concentrations have been omitted for the sake of clarity.

Extraction of copper

In the initial experiments it appeared that equilibrium was not established after a short period of shaking but was only approached after 24 hours agitation. It was further noted that after this period the solutions had lost their characteristic dark colour, becoming in fact, pale green and that the organic phase had acquired lachrymatory properties. In subsidiary investigations it was shown that most of the copper had been reduced to the cuprous state, whilst the ketone had brominated. This effect was most marked with MEK as can be seen from Fig. 1, where the extraction curves for cuprous and cupric copper are practically coincident at the higher concentrations of ammonium bromide. Such behaviour can no doubt be attributed to the reactivity of the methylene group in MEK being greater than that of the methylene group in MIBK, as this is very probably the part of the ketone molecule where substitution bromination occurs. The divergence of the two sets of curves mentioned above, at the lower concentrations of ammonium bromide can be attributed to the slower speed of reduction of the copper at these concentrations.

Further evidence of the greater susceptibility of MEK to bromination is provided by a comparison of cupric bromide extractions over periods of 24 hours and 5 minutes, with the two solvents. These extractions are illustrated in Figs. 1 and 2, where it will be observed that although higher acid concentrations were employed in the MIBK experiments, the 5 minute curve lies much closer to the 24 hour curve than for the case of MEK, showing that less reduction of the copper occurs with MIBK over a given period of time.

0.05M solutions of cuprous bromide were used in the above extractions so that the total amounts of copper in the Cu(II) and Cu(I) systems would be the same.

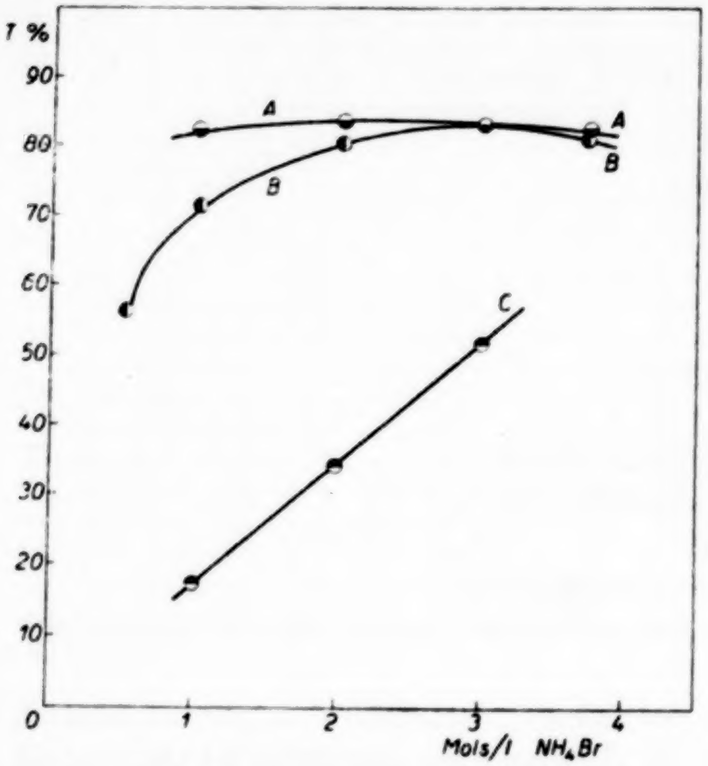

Fig. 1. Extraction of copper with MEK. Initial aqueous solutions contain 0.76M HBr. 0.1M CuBr$_2$ 24 hours (B), 5 minutes (C). 0.05M Cu$_2$Br$_2$ (A).

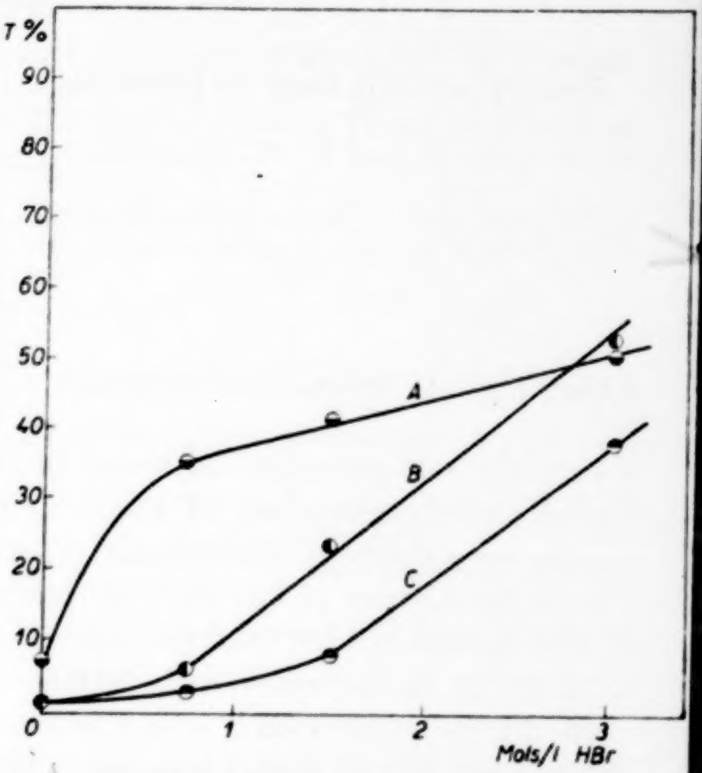

Fig. 2. Extraction of copper with MIBK. Initial aqueous solutions contain 2.0M NH$_4$Br. 0.1M CuBr$_2$ 24 hours (B), 5 minutes (C). 0.05M Cu$_2$Br$_2$ (A).

The extraction experiments of 5 minutes duration with cupric bromide were carried out in order to gain a clearer idea of the true extraction behaviour of cupric copper in the absence of reduction reactions. It was, however, noticed that even after 5 minutes some reduction had occurred thus rendering the results for the extraction of copper slightly inaccurate.

The bromination of the ketones in the above experiments was considered to be unusual, but it was thought that this behaviour might be accounted for by an electron transfer reaction catalyzed by one or more of the components in the system. This issue was subsidiary to the main problem and after carrying out some dark experiments to ensure that the reaction was not photoactivated the investigation of copper bromide was abandoned.

Extraction of zinc

TABLE I

EXTRACTION OF 0.1M ZnBr$_2$ WITH MIBK

NH$_4$Br M	HBr M	E	T%
1.0	0	0.049	4.6
2.0	0	0.082	7.5
3.0	0	0.095	8.6
4.0	0	0.090	8.2
1.0	0.76	0.128	11.2
2.0	0.76	0.192	16.0
3.0	0.76	0.180	15.0
4.0	0.76	0.138	12.0

TABLE II

EXTRACTION OF 0.1 M $ZnBr_2$ WITH MIBK

Initial solutions contain 2.0 M NH_4Br

HBr M	E	T%
0.00	0.081	7.5
0.76	0.192	16.0
1.52	0.321	24.1
3.04	0.664	39.1
3.80	1.052	50.5

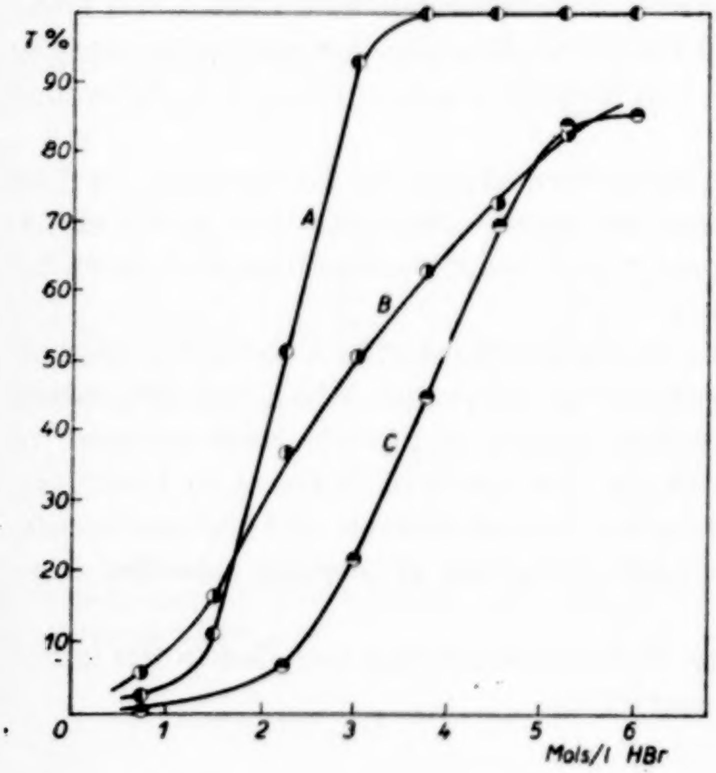

Fig. 3. Extraction of cupric, zinc and ferric bromides from hydrobromic acid solution with MIBK. $CuBr_2$ (C), $ZnBr_2$ (B), $FeBr_3$ (A).

The curve for the extraction of zinc from hydrobromic acid solutions, Fig. 3, shows that it is very similar in behaviour to Cu(II) as was noticed in extractions with ether[2], although in this latter solvent both metals were extracted to the extent of a few per cent only. The linear dependance on hydrobromic acid concentration of percentage extraction of zinc in the presence of a fixed concentration of ammonium bromide (Table II) is noteworthy. It is unusual to note such linearity over such a wide range of acid concentration.

Extraction of ferric iron

TABLE III

EXTRACTION OF 0.1 M $FeBr_3$ WITH MIBK

NH_4Br M	HBr M	E	T%
1.0	0	0.016	1.6
2.0	0	0.028	2.8
3.0	0	0.072	6.7
4.0	0	0.348	25.8
1.0	0.76	0.066	6.1
2.0	0.76	0.317	24.0
3.0	0.76	1.34	57.6
4.0	0.76	6.96	87.7

TABLE IV

EXTRACTION OF 0.1M $FeBr_3$ WITH MIBK

Initial solutions contain 2.0M NH_4Br.

HBr M	E	T%
0.00	0.028	2.8
0.76	0.317	24.0
1.52	3.20	76.2
3.04	∞	100.0
3.80	∞	100.0

It will be noticed that at low concentrations of hydrobromic acid (Table III) ferric bromide is much more efficiently extracted than zinc. It is also interesting to note the steepness of the curves in Table IV and Fig. 3 at medium concentrations of hydrobromic acid.

Although ferric ions form ion pairs and have been shown by EVANS AND URI[4] to produce radicals when irradiated, on shaking the higher complexes used in the distribution experiments with MEK for 24 hours it was found that no bromination of the ketone had occured, as in the case of copper.

In the extraction of ferric bromide from aqueous solutions of hydrobromic acid there is a similarity with BOCK's results[2], the shapes of the curves for MIBK and ether being very alike. The MIBK results would therefore appear to provide some measure of support for BOCK's suggested explanation of the low result of WADA AND ISHII[5] *viz.* "partial decomposition of the aqueous solution into ferrous bromide and bromine occurs, a reaction which is promoted by the extensive extraction of bromine into the ether phase."

In this work as in that of BOCK an excess of free bromine was included in the initial aqueous solutions to depress the above dissociation.

Extraction of tin

TABLE V

EXTRACTION OF 0.1M $SnCl_2$ WITH MIBK

Initial solutions contain 0.76M HBr.

NH_4Br M	E	T %
0.0	3.55	78.3
1.0	7.61	88.6
2.0	7.16	88.1
3.0	5.69	85.2
4.0	3.77	79.4

Once again in the extraction of tin bromides there is a similarity in the results for the extraction of stannous tin and stannic tin from hydrobromic acid solution by MIBK with **Bock**'s results for the extraction with ether of these two bromides[2]. He observed coincident maxima in the extraction curves at an approximate concentration of $4M$ hydrobromic acid, above which the curves themselves were coincident. It can be seen from Fig. 4 that the same behaviour is apparent with MIBK, although the maxima are flatter and higher, but coincidence once again occurs at an acid concentration of approximately $4M$. This type of behaviour is again shown in Tables VI and VIII, where hydrobromic acid is the variant, but it is not apparent in Tables V and VII where the concentration of acid is fixed and the ammonium bromide concentration is the variant.

TABLE VI

EXTRACTION OF $0.1M$ $SnCl_2$ WITH MIBK

Initial solutions contain $2.0M$ NH_4Br.

HBr M	E	T %
0.76	7.16	88.1
1.52	15.28	93.9
2.28	24.28	96.0
3.04	31.80	97.0
3.80	40.10	97.6

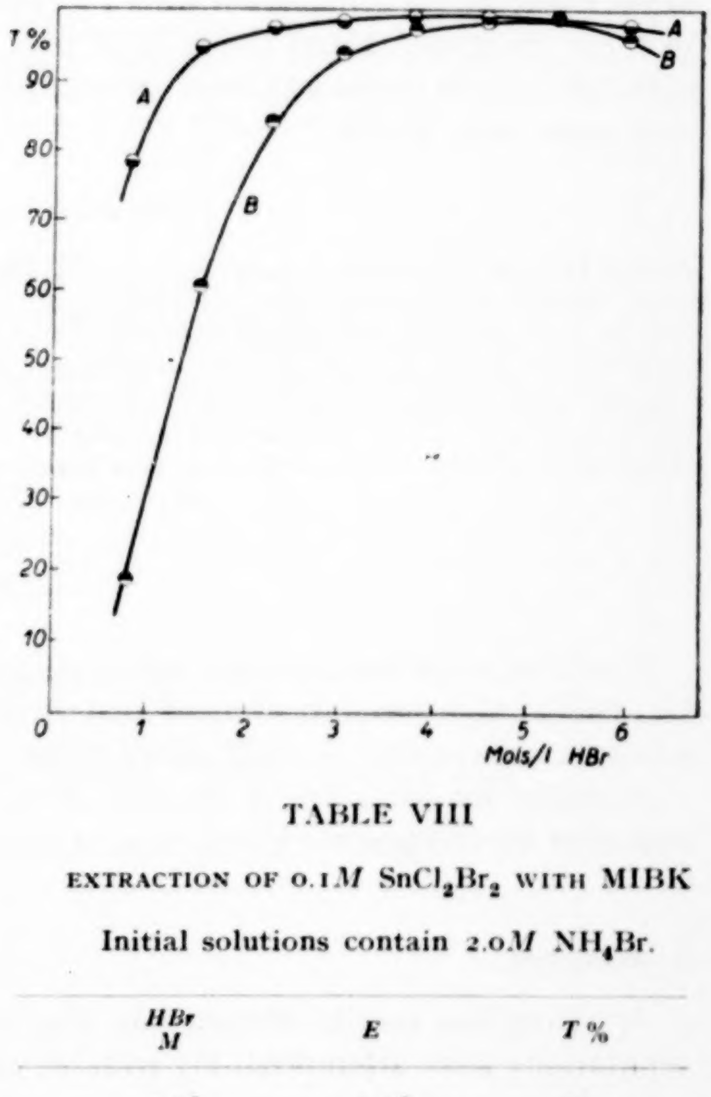

Fig. 4. Extraction of stannous and stannic tin from hydrobromic acid solution with MIBK. $SnCl_2$ (A), $SnCl_2Br_2$ (B).

TABLE VII

EXTRACTION OF $0.1M$ $SnCl_2Br_2$ WITH MIBK

Initial solutions contain $0.76M$ HBr.

NH_4Br M	E	T %
0.0	0.232	18.8
1.0	1.061	51.7
2.0	2.56	72.3
3.0	4.97	83.8
4.0	7.88	89.1

TABLE VIII

EXTRACTION OF $0.1M$ $SnCl_2Br_2$ WITH MIBK

Initial solutions contain $2.0M$ NH_4Br.

HBr M	E	T %
0.76	2.56	72.3
1.52	7.66	88.8
2.28	18.46	95.0
3.04	40.05	97.7
3.80	65.20	98.6

Extraction of ferrous iron and aluminium

It was found impossible to extract either ferrous iron or aluminium from aqueous solutions containing high concentrations of hydrobromic acid and ammonium bromide with MIBK.

Extraction of manganese, nickel and cobalt

Manganese is only extracted when high concentrations of both ammonium bromide and hydrobromic acid are present in the initial aqueous solutions and then only to the extent of about 14%.

Only an infinitesimal amount of cobalt is extracted by MIBK and only at high concentrations of ammonium bromide and hydrobromic acid.

Nickel is extracted to the extent of a few per cent under similar conditions.

Extracted species

In an attempt to discover the form in which the iron was extracted the organic phases of the experiments listed below were analysed for bromide. The iron was 100% extracted in these experiments and the ratio of iron: bromine present in the organic phase was calculated. This ratio was then corrected from data on the extraction of hydrobromic acid alone into MIBK.

TABLE IX

$FeBr_3$ M	HBr M	Fe : Br	Fe : Br corr.
0.2	3.80	1:3.90	1:3.90
0.2	4.56	1:4.46	1:3.96
0.2	5.32	1:5.20	1:3.40

It will be noted that the last ratio appears to be overcorrected but this is due to the fact that at high concentrations of acid there is some interaction between acid and ketone which interferes with normal distribution.

A similar investigation in the case of the extraction of zinc with MEK was rendered valueless by the greater interaction of hydrobromic acid with MEK.

Separations

Applying the results obtained in the investigation of the individual metals some separations were attempted. By suitable choice of conditions it was found possible to separate completely in one extraction ferric iron from manganese, ferric iron from aluminium and ferric iron from cobalt. Also it should be possible virtually to separate ferric iron from nickel with one extraction into MIBK followed by a back extraction of the solvent with hydrobromic acid solution.

In conclusion it may be said that this investigation has shown that MIBK is a more useful solvent than MEK by virtue of its greater scope, whereby higher concentrations of acid may be used, resulting in more efficient extractions.

In comparison with BOCK's results for ether[2] the metals extracted with MIBK show the same degrees of difference of behaviour between themselves but seem to be more efficiently extracted by the ketone.

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SUMMARY

The extraction of the following metals from aqueous solutions containing excess bromide with methyl ethyl ketone (MEK), and methyl *iso*butyl ketone MIBK has been investigated: —
Cu(I), Cu(II), Zn(II), Ni(II), Co(II), Fe(II), Fe(III), Al(III), Mn(II), Sn(II) and Sn(IV).
The use of MEK was found to be strictly limited by its solubility in acidic aqueous solutions. Determinations of the formulae of the extracted compounds were attempted in two cases but were found to be not wholly satisfactory and were discontinued. An interesting reaction between the cupric bromide complex and the solvents was noticed. Separations of Fe(III) from Mn(II), Fe(III) from Al(III), Fe(III) from Co(II) and Fe(III) from Ni(II) could be achieved under suitable conditions.

RÉSUMÉ

L'extraction des cations suivants: Cu(I) et (II), Zn, Ni(II), Co(II), Fe(II) et (III), Al, Mn(II), Sn(II) et (IV) a été examinée en solution aqueuse en présence d'un excès de bromure, au moyen de méthyléthylcétone et de méthyl*iso*butylcétone. L'emploi de méthyléthylcétone est strictement limité, par sa solubilité, à des solutions aqueuses acides. Les auteurs ont essayé en vain de déterminer les formules des composés extraits dans ces deux solvants. Une réaction intéressante est signalée entre le bromure de cuivre(II) et les solvants. Les séparations suivantes: Fe(III) de Mn(II), Fe(III) de Al(III), Fe(III) de Co(II) et Fe(III) de Ni(II), peuvent être effectuées.

ZUSAMMENFASSUNG

Die Extraktion der folgenden Kationen: Cu(I) und (II), Zn, Ni(II), Co(II), Fe(II) und (III), Al, Mn(II), Sn(II) und (IV) wurde in einer wässrigen Lösung in Gegenwart eines Überschusses an Bromid untersucht, mit Hilfe von Methyläthylketon und Methyl*iso*butylketon. Die Verwendung von Methyläthylketon ist wegen seiner Löslichkeit streng begrenzt für saure wässrige Lösungen. Die Autoren haben vergeblich versucht, die Formeln der ausgezogenen Verbindungen in diesen zwei Lösungsmitteln zu bestimmen. Es wird eine interessante Reaktion zwischen Kupfer(II) bromid und den Lösungsmitteln gezeigt. Es können folgende Trennungen vorgenommen werden: Fe(III) von Mn(II), Fe(III) von Al(III), Fe(III) von Co(II) und Fe(III) von Ni(II).

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EFFECT OF THE DISTANCE MOVED BY THE SOLVENT ON THE R_F VALUES IN CIRCULAR CHROMATOGRAPHY *

by

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RAO AND GIRI[1], while studying the dependence of R_F value on the distance moved by the solvent in their experiments on circular paper chromatography observed that the R_F values of the amino acids at first increase with the distance travelled by the solvent from 5 cm to 10 cm and then decrease as the distance is increased from 10 cm to 15 cm. The decrease in R_F values with increasing distance may be accounted for by the gradual loss of the acid as well as the water contents as the developing solvent moves[1,2], but the increase in R_F values could not be explained. According to the partition mechanism of paper chromatography[3] the R_F values should be fairly independent of the distance moved by the solvent; this was found to be so[4] in case of strip chromatography, though KOWKABANY AND CASSIDY[5] observed that there was slight increase in R_F values up to a point.

The R_F values of the amino acids given by RAO AND BERI[6], also on the basis of circular paper chromatograms are much higher than those obtained by GIRI[7], and RAO AND GIRI[1] have contradicted the former. The reproducibility of the R_F values are known to depend upon a number of factors but more often in experiments using less volatile solvents, the R_F values obtained by different workers agree fairly well with one another. In this context the contradictory nature of the findings of RAO AND BERI[6] and of GIRI[7] and RAO AND GIRI[1] should be more carefully looked into. It appeared that the above authors[1,6,7] have not taken sufficient cognisance of the importance of maintaining saturation in the chamber. Since unsaturation has been shown to affect the measurements markedly, it was considered advisable to study further the effect of the distance moved by the solvent on the R_F values. For this purpose, a carefully airtight equipment as described below was used.

EXPERIMENTAL

The equipment is simple and inexpensive as Fig. 1 will show. It consists of a circular glass trough A and a lid B with a central small opening C (as shown in Fig. 1). Both were ground at the edges and applied with desiccator grease to ensure airtightness. The trough contains a suitable amount of the solvent to ensure saturation. Inside the trough a circular glass ring D is resting on three short legs; this ring supports a slightly bigger filter paper E, on which the desired chromatogram is to be obtained. A petri dish F is kept in position at the centre of the trough by means of the glass tube G so that the rim of the dish does not touch the paper E. The tube G passes through a small circular

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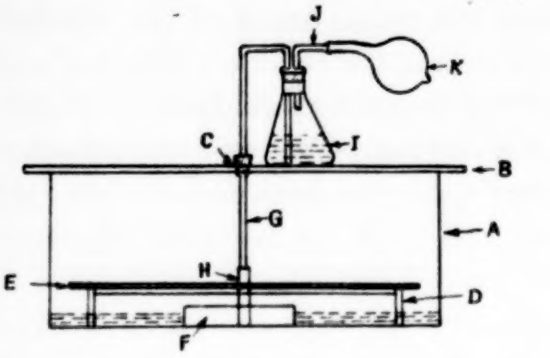

Fig. 1. Special arrangement for circular paper chromatography.

opening H at the centre of the paper E and then through the tight fitting cork at the centre C of the lid. At the top end it is connected to an arrangement for the transfer of the developing solvent from the reservoir I to the petri dish F. The transfer is done with the help of a blower K placed at the opening of the tube J, which is otherwise kept closed during the experiment. The lower part of the tube G—from the petri dish up to a certain distance above the paper E—is wrapped with a piece of filter paper which serves as the wick for the development of the circular chromatogram.

After applying the amino acid solutions and subsequent drying, the circular paper is placed in position as shown in the figure. It is then allowed to equilibrate for 24 hours with the saturating vapours inside the perfectly airtight chamber. Then the cork at the end of the tube J is temporarily replaced by a blower K and the blower is pressed once. Once the developing solvent is forced into the petri dish, the whole of it is transferred by siphon action from I to F. Development of the chromatogram starts immediately and the blower is replaced at J by the cork which closes it. After the solvent travels up to the desired distance the paper is taken out and the usual method of indication is followed.

RESULTS

Table I records the R_F values of a number of amino acids with the solvent butanol-acetic acid-water which has been allowed to travel varying distances. In these experiments each amino acid was applied, as with Rao and Giri[1], at the centre of the paper and was separately run.

TABLE I

Developing solvent — Upper layer of butanol-acetic acid-water (4 : 1 : 5)
(without temperature control)
N.B. Amino acid solutions were applied at the centre of the paper

Amino acids	*Distance travelled by the solvent*		
	5 cm	10 cm	15 cm
Aspartic acid	0.41	0.40	0.41
Glutamic acid	0.45	0.44	0.43
Alanine	0.56	0.52	0.50
Valine	0.64	0.60	0.58
Leucine	0.74	0.70	0.69

For those given in Tables II-IV a number of amino acids were simultaneously but individually developed by applying them on a circular orbit (diameter 2 cm) at the centre of the paper in such a way that one was slightly apart from the other. The available glass trough enabled the maximum distance that the solvent could be allowed to travel to be 13 cm. The values were therefore recorded corresponding to the distances 4, 8 and 12 cm. Rao and Giri[1], it may be mentioned, recorded the R_F values corresponding to 5, 10 and 15 cm.

The R_F values of some of the amino acids obtained in this way using respectively phenol saturated with water and butanol-acetic acid-water are given in Tables II and III. Phenol being a less volatile solvent, a set of values was also determined for comparison, in which no care was taken to maintain saturation inside the chamber.

With butanol-acetic acid-water again, two sets of data were obtained. Those recorded in Table III were obtained at room temperature using the upper layer of the partially miscible mixture in the ratio 4:1:5. A single phase is formed in the ratio 4:1:1 of butanol-acetic acid-water up to about 20° C[9]. This was used for the determination of the R_F values at the controlled temperature (26.0 ± 0.5° C), since temperature is an important factor even in case of miscible solvents[8]. The observed data are recorded in Table IV.

TABLE II

Developing solvent — Phenol saturated with water
(without temperature control)

Amino acids	*Distance travelled by the solvent*		
	(a) without saturation		
	4 cm	8 cm	12 cm
Aspartic acid	0.34	0.36	0.35
Glutamic acid	0.48	0.44	0.49
Serine	0.52	0.52	0.54
Glycine	0.57	0.59	0.58
Threonine	0.63	0.63	0.63
Alanine	0.75	0.76	0.79
Valine	0.84	0.84	0.84
Phenylalanine	0.92	0.92	0.90
	(b) with saturation		
Aspartic acid	0.26	0.28	0.30
Glycine	0.45	0.47	0.46
Alanine	0.58	0.60	0.60
Valine	0.75	0.74	0.72
Methionine	0.81	0.80	0.80
Phenylalanine	0.90	0.88	0.87

TABLE III

Developing solvent — Upper layer of butanol-acetic acid-water (4 : 1 : 5)
(without temperature control)

Amino acids	*Distance travelled by the solvent*		
	4 cm	8 cm	12 cm
Cystine HCl*	0.19	0.18	0.18
Histidine HCl*	0.28	0.24	0.24
Aspartic acid	0.33	0.35	0.34
Glutamic acid	0.35	0.33	0.35
Glycine	0.36	0.36	0.36
Alanine	0.48	0.48	0.45
Valine	0.56	0.53	0.52
Phenylalanine	0.71	0.66	0.66

TABLE IV

Developing solvent — Butanol-acetic acid-water (4 : 1 : 1)
(temperature controlled at 26 ± 0.5° C)

Amino acids	*Distance travelled by the solvent*		
	4 cm	8 cm	12 cm
Aspartic acid	0.31	0.31	0.32
Glycine	0.32	0.33	0.34
Alanine	0.44	0.47	0.45
Valine	0.59	0.58	0.57
Methionine	0.60	0.59	0.58
Phenylalanine	0.73	0.72	0.70

* Applied as hydrochloride and neutralized with NH_3

DISCUSSION

It is clear from Tables I-IV that the R_F values are almost independent of distance travelled by the solvent. The discrepancies are fairly within experimental variations and are mostly due to some unavoidable experimental procedure. For instance, the observed decrease in R_F with the increase of the distance travelled by the solvent, as specially evident from Table I may be accounted for by the gradual loss of the acid-content as well as the water-content of the developing solvent. Perfect saturation of the chamber being assured, the R_F values under otherwise similar conditions do not show any increase as the solvent distance increases from 5 cm to 10 cm. If saturation is not rigorously attended to, the variation in R_F may be envisaged as follows. At the start the solvent moves very quickly and in spite of unsaturation inside the chamber almost normal values are obtained. In the next stage, however, (5 cm — 10 cm) unsaturation increases the R_F values, since owing to loss of solvent from the moving front, the apparent distance travelled becomes less than the actual distance. In the third stage (10 cm — 15 cm) the system becomes almost saturated at the expense of loss in the previous stage and thereby normal values are again obtained. A situation such as the above probably existed in the experiments of RAO AND GIRI[1], which explains the observed variation in R_F. It should be pointed out here that the R_F values obtained on a circular chromatogram with the solvents phenol-water and butanol-acetic acid-water are in most cases in fair agreement with those presented by RAO AND GIRI[1]. In certain cases the values obtained by RAO AND GIRI[1] appear to be a bit higher but not as high as those obtained by RAO AND BERI[6]. The conclusion seems obvious from the above observations that the very high values obtained by RAO AND BERI[6] were due to lack of necessary saturation in the chamber. For purposes of separation the R_F values are of little concern and hence to avoid confusion the relative position of the solutes on the chromatogram may only be noted when the necessary conditions for their measurements are not strictly controlled.

The R_F values with phenol-water, as recorded in Table II(a) are somewhat in agreement with those obtained by RAO AND GIRI[1] as well as those reported by the authors in a previous publication[10]. The divergences become wide in the case of low R_F values. With the saturation of the chamber, all the R_F values are lowered, the previously low ones being affected the most (of Table II(b)). The necessity of maintaining perfect saturation becomes therefore obvious.

Another peculiarity is observed in comparing the values recorded in Tables I and III. The rates of travel of amino acids, applied on a circle of diameter 2 cm at the centre, are less than those of the amino acids applied just at the centre and individually developed. In the former case the amino acids appear along arcs on the chromatogram whereas in the latter full circles are formed. The differences in the observed rates of travel may be due to different radial forces operating in the two cases, which, it has been previously shown by the authors[10], alter the R_F values. For instance an increase in the radial force causes the R_F values to increase.

During the experiments with varying distances travelled by the solvent front the solute is applied at the same starting point, so it passes through different phase compositions and does not abruptly face a phase composition entirely different from other sets of experiments. Even for varying distances travelled by solvent, the solute at first experiences the same phase compositions, towards the end, however, these compositions begin to vary. Since R_F values in these cases are an average of R_F values at the different stages, influence of this change of phase compositions is not reflected much in the R_F values. But if there is considerable difference between the two distances travelled (say 5 cm and 30 cm) the R_F values must decrease with increase of distance.

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Our thanks are due to Dr. D. M. BOSE, Director, Bose Institute, for his kind interest and to Dr. S. K. MUKHERJEE, Lecturer, University College of Science and Technology, Calcutta, for criticism and discussion.

SUMMARY

1. The effect of the distance travelled by the solvent on the R_F values of the amino acids subjected to circular paper chromatography has been studied under various conditions with two solvents; (i) Phenol-water, which is less volatile and (ii) butanol-acetic acid-water which is more volatile. The R_F values with both the solvents are almost independent of the distance travelled by the solvent. It is essential in all these experiments to control perfect saturation inside the chamber in order to get reproducible R_F values.

2. The increase in R_F values reported by RAO AND GIRI[1] with distance of travel of the solvent appears to be due to lack of necessary saturation inside the chamber. The same defect seems to have vitiated the experiments of RAO AND BERI[6] who also reported very high R_F values.

3. Butanol-acetic acid-water of the composition 4 : 1 : 1[9] is suggested as a good solvent for practical purposes.

RÉSUMÉ

1. L'effet de la distance traversée par le solvant, sur les valeurs de R_F des amino-acides, par chromatographie circulaire sur papier, a été étudié dans diverses conditions, à l'aide de deux solvants: (i) phénol-eau qui est moins volatile et (ii) butanol-acide acétique-eau, plus volatile. Les valeurs de R_F obtenues avec ces deux solvants sont à peu près indépendantes de la distance traversée par le solvant. Il est essentiel dans toutes ces expériences de contrôler la parfaite saturation du milieu ambiant pour obtenir des valeurs de R_F reproductibles.

2. L'augmentation des valeurs de R_F avec l'étendue de diffusion des solvants signalée par RAO ET GIRI[1], due à la distance semble être due à une saturation insuffisante du milieu. Ceci expliquerait également les valeurs de R_F très élevées trouvées par RAO ET BERI[6].

3. Le mélange butanol-acide acétique-eau, de composition 4 : 1 : 1[9], est considéré comme un bon solvant.

ZUSAMMENFASSUNG

1. Der Einfluss der Distanz, welche vom Lösungsmittel durchlaufen wird, auf die Werte für R_F der Aminosäuren bei der kreisförmigen Papierchromatographie wurde untersucht unter verschiedenen Bedingungen mit Hilfe von 2 Lösungsmitteln: (i) Phenol-Wasser, welches weniger flüchtig ist und (ii) Butanol-Essigsäure-Wasser, welches flüchtiger ist. Die, mit diesen zwei Lösungsmitteln erhaltenen R_F-Werte, sind ungefähr unabhängig von der vom Lösungsmittel durchlaufenen Distanz. Bei allen Experimenten ist es wichtig, die vollständige Sättigung des umgebenden Milieus zu kontrollieren, um reproduzierbare R_F-Werte zu erhalten.

2. Die Zunahme der R_F-Werte mit zunehmender Diffusionsstrecke der Lösungsmittel, welche von RAO UND GIRI[1] angegeben werden, scheint die Folge von einer ungenügenden Sättigung des Milieus zu sein. Dies würde auch die hohen R_F-Werte erklären, welche von RAO UND BERI[6] gefunden wurden.

3. Das Mischungsverhältnis Butanol-Essigsäure-Wasser 4 : 1 : 1[9], wird als gutes Lösungsmittel betrachtet.

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THE CHROMATOGRAPHIC EXAMINATION OF METALLIC IONS, I

by

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INTRODUCTION

As a prelude to the chromatographic investigation of certain metallic complexes, it was necessary to determine the R_F values of a number of metal ions, using as solvent butanol saturated with individual aqueous solutions of several organic acids. The results obtained indicated that some of the solvents employed could be applied to the qualitative separation of some cation mixtures. The possibility of quantitative separations was also indicated in some cases.

TABLE I

Developing reagent: H_2S and NH_3

Solvent: Butanol saturated with: —	*R_F values of ions*											
	Fe^{II}	*Fe^{III}*	*Co^{II}*	*Ni^{II}*	*Ir^{II}*	*Ir^{IV}*	*Mo^{IV}*	*Pt^{II}*	*Pt^{IV}*	*Ru^{IV}*	*Tl^{I}*	*Pd^{II}*
1.0*M* Thioglycollic acid	0.02	0.02	0.03	0.04	0.04	0.05	0.64	0.60 T to L.F.	T to L.F.	0.03 T to 0.51	0.10	0.92 T
1.0*M* Dithicglycollic acid	0.03	0.05	0.03	0.03	Nil	Nil	0.15 T	0.63 T to L.F.	0.56 T to L.F.	0.03	0.12	0.68 T to L.F.
1.0*M* Citric acid	Nil	Nil	0.05	0.04	Nil	Nil	0.30 T	0.54	0.60	0.04 T to 0.58	0.11	0.54
1.0*M* Tartaric acid	0.03	0.03	0.08	0.03	0.04	0.03	0.38 T	0.46 T to 0.62	0.58	0.08	0.09	0.50
1.0*M* Lactic acid	0.20	0.09	0.04	0.05	0.03	0.02	0.44	T to 0.58	0.57	0.06 T to 0.60	0.12	0.50
1.0*M* Malonic acid	0.04	0.03	0.05	0.06	Nil	Nil	0.08 T to 0.50	0.57 T	0.64 T	0.04 T to 0.62	0.14	0.56 T
Saturated aqueous solution of ethylenediamine tetra-acetic acid	Nil	Nil	0.03	0.02	Nil	Nil	0.10 T to 0.54	T to 0.52	0.52 T	0.05	0.06	0.52
1.0*M* Salicylic acid	T to 0.18	T to 0.12	0.02 T to 0.50	0.02	0.03 T to 0.12	0.03	0.28	0.11 T	0.50 T	T to 0.50	0.06	0.35 T
1.0*M* Oxalic acid	0.04	0.08	0.02	0.03	0.04	0.02	0.54	0.28 T to 0.56	0.56	0.01 T to 0.58	0.08	0.52
1.0*M* Succinic acid	0.01	0.01	0.06	0.06	0.05	0.02	0.08	0.55 T to 0.78	0.64 T	0.16 T to 0.60	0.15	0.57 T
Water	Nil	Nil	0.03	0.03	Nil	Nil	0.08 T to 0.46	0.58 T	0.56 T	0.05 T to 0.56	0.06	0.44 T

T: Trails
L.F.: Liquid front

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EXPERIMENTAL

Approximately 0.02 ml of 0.1*M* solutions of the ions were spotted on to sheets of Whatman's No. 40 filter paper and the chromatograms run in covered ground glass Winchester bottles, 6 inches in diameter and 10 inches in height, which contained both phases of the solvent mixture. The ascending technique was employed[1]. The sheets were air-dried and then exposed to H_2S or sprayed with the appropriate developing reagent. The R_F values obtained are shown in Tables I, II, and III.

TABLE II

Developing reagent: H_2S

Solvent: Butanol saturated with: —	*R_F values of ions*											
	Cd^{II}	*Hg^{I}*	*Hg^{II}*	*Sn^{II}*	*Sn^{IV}*	*Pb^{II}*	*As^{III}*	*Sb^{III}*	*Bi^{III}*	*Cu^{II}*	*Ag^{I}*	*Au^{III}*
1.0*M* Thioglycollic acid	0.01	T to 0.90	T to 0.90	0.66	0.67	0.01	0.93 to L. F.	0.77	0.68 T	0.02	0.01	to 0.60
1.0*M* Dithioglycollic acid	Nil	0.06	0.78 T	0.66	0.72	0.05	0.54	0.64	0.18 T	0.06 T to 0.16	0.36	0.31 T to 0.84
1.0*M* Citric acid	0.03	0.11	0.74	0.63	0.64	0.05	0.43	0.57	0.06 T	0.10	0.14	0.79 T and R
1.0*M* Tartaric acid	0.03	0.36 T	0.74	0.73 T	0.64	0.03	0.46	0.62	0.53 T	0.02	0.09	0.92 T and R
1.0*M* Lactic acid	Nil	T to 0.28	0.72	0.64	0.62	0.10	0.43	0.60	0.16	0.19	0.10	0.85 T and R
1.0*M* Malonic acid	0.02	0.12 T to 0.77	0.77	0.66	0.64	0.07	0.48	0.61	0.08 T	0.06	0.14	0.79 T
Saturated aqueous solution of ethylenediamine tetra-acetic acid	Nil	0.20 T	0.73	0.58	0.62	0.04	0.42	0.60	0.03 T	0.07	0.08 T	T to 0.80
1.0*M* Salicylic acid	Nil	T to 0.54	0.64	0.58	0.56	0.04 T to 0.36	0.47	0.52	0.30	0.11 T to 0.52	0.08	0.75
1.0*M* Oxalic acid	Nil	0.05	0.75	0.68	0.68	Nil	0.50	0.60	0.03	0.02	0.01	0.86 T and R
1.0*M* Succinic acid	Nil	T to 0.41	0.78	0.73	0.66	0.07	0.47	0.60	0.28	0.13	0.18	0.90 T and R
Water	Nil	0.20 T	0.74	0.62	0.56	0.04	0.46	0.60	0.06 T	0.08	0.10	0.84 T and R

T: Trails; L.F.: Liquid front; R: Reduction occurs

DISCUSSION

As a result of the work carried out, the following general observations may be made: —

(a) Comparatively few ions moved to any extent in the solvents employed.

(b) Some distinct separations were noted: —

(i) The separation of Hg^{I} and Hg^{II} may be effected with all the solvents used except in the case of butanol saturated with 1.0*M* solutions of thioglycollic, malonic and salicylic acids.

TABLE III

Developing reagent: Alcoholic solution of 8-hydroxyquinoline and kojic acid followed, after air-drying, by exposure to ammonia and to ultra-violet light

Solvent: Butanol saturated with: —	R_F values of ions																			
	Be^{II}	Mg^{II}	Ca^{II}	Sr^{II}	Ba^{II}	Zn^{II}	Al^{III}	In^{III}	Tl^{III}	Ti^{IV}	Th^{IV}	VO^{II}	Cr^{III}	Mo^{VI}	W^{VI}	UO_2^{II}	Ce^{III}	Ce^{IV}	Mn^{II}	Ga^{III}
1.0*M* Thioglycollic acid	0.15	Nil	Nil	Nil	Nil	Nil	0.03	0.18	0.10	0.01	0.19	0.02	Nil	0.10	0.06	0.26	0.04	0.04	0.02	0.13
1.0*M* Dithioglycollic acid	0.20	Nil	0.04	0.02	0.05	Nil	0.06	0.15	0.88	0.04	0.07	0.02	Nil	0.05	Nil	0.32	Nil	0.04	0.03	0.10
1.0*M* Citric acid	0.14	Nil	—	—	—	Nil	0.06	0.18	0.84	0.16	0.03	0.06	Nil	0.06	Nil	0.08	Nil	0.02	0.05	0.06
1.0*M* Tartaric acid	0.10	Nil	0.03	0.03	—	0.06 and 0.52	0.02	0.14	0.87	0.35 T	Nil	0.04	0.03	0.36	0.01	0.08	Nil	0.06	0.03	0.02
1.0*M* Lactic acid	0.22	Nil	0.03	0.03 T to 0.35	0.05 T to 0.24	Nil	0.12	0.22	0.86	0.24 T	0.10	0.05	Nil	0.06	Nil	0.34	0.06	0.03	0.06	0.24
1.0*M* Malonic acid	0.20	0.01	0.03	—	—	Nil	0.04	0.15	0.86	0.03	0.02	0.05	Nil	0.06	Nil	0.19	0.04	0.02	0.05	0.05
Saturated aqueous solution of ethylenediamine tetraacetic acid	0.10	Nil	Nil	0.02	0.02	Nil	0.02	0.13	0.82	0.01	0.02	0.02	Nil	0.02	0.01	0.10	0.03	0.01	0.03	0.07
1.0*M* Salicylic acid	0.17	0.01	0.03	0.01	0.01	Nil	0.04	0.11	0.77	0.26	0.16	0.02	Nil	0.10	Nil	0.26 and 0.92	0.04	0.01	0.03	0.10
1.0*M* Oxalic acid	0.18	0.02	0.04	—	—	Nil	0.05	0.12	0.90	0.30 T	Nil	0.14	Nil	0.39	0.05	0.28	Nil	0.02	0.02	0.14
1.0*M* Succinic acid	0.22	Nil	0.03	0.03	0.03	Nil	0.04	0.18	0.88	0.04	0.06	0.02	Nil	0.06	Nil	0.30	0.06	Nil	0.05	0.02
Water	0.10	0.01	0.02	0.03	0.03	Nil	0.02	0.12	0.81	0.04	0.01	0.01	Nil	0.01	Nil	0.16	0.03	0.03	0.03	0.02

T: Trails; —: Not detected

(ii) The separation of Tl^I from Tl^{III} may be readily effected with all the solvents used, except butanol saturated with 1.0*M* thioglycollic acid.

(iii) Uranyl ion may be separated from many ions by means of butanol saturated with 1.0*M* aqueous solutions of salicylic, thioglycollic, dithioglycollic, lactic, oxalic and succinic acids.

(iv) Ag^I may be separated from many other metal ions by means of butanol saturated with 1.0*M* dithioglycollic acid.

(v) The use of butanol saturated with 1.0*M* thioglycollic acid or with 1.0*M* oxalic acid enables the Mo^{IV} ion to be separated from some cation mixtures.

(vi) The high R_F value of As^{III} permits of its separation from most other ions when butanol saturated with 1.0*M* thioglycollic acid is used as solvent. This occurred to a lesser extent with both Sb^{III} and Bi^{III} in this solvent.

(c) The formation of two distinct spots was noted in the case of Zn^{II} when butanol saturated with 1.0*M* tartaric acid was used as solvent, and with UO_2^{II} using butanol saturated with 1.0*M* salicylic acid, followed, in each case, by spraying with an alcoholic solution of 8-hydroxyquinoline and kojic acid and exposure to ammonia and ultra-violet light.

(d) Using butanol saturated with water only as solvent, it was found that Hg^{II}, Tl^{III}, Sn^{II}, Sn^{IV}, As^{III}, Sb^{III}, Pd^{II}, Pt^{II}, Pt^{IV} and Au^{III}, moved approximately to the same extent as with the other solvents. It would appear that this is due to the greater stability of the complexes of the above ions with the ligand in the original solution of the ion than their complexes with the anion in the solvent employed. This point is the subject of further investigation.

(e) Considerable adsorption of acid takes place on the cellulose, resulting in the appearance of a second liquid front, lower than the first liquid front. This phenomenon has also been observed by other workers[3,4,5]. For reasons given below, it is suggested that this be called the "adsorption front". For the majority of the solutions employed, this value, in terms of R_F value, has been noted, and the results obtained are shown in Table IV.

TABLE IV

Acid employed	*R_F value of acid front*	*Number of -OH groups in acid employed*	*Number of -COOH groups in acid employed*
Tartaric	0.37	2	2
Citric	0.56	1	3
Lactic	0.70	1	1
Oxalic	0.72	—	2
Malonic	0.75	—	2
Succinic	0.82	—	2
Dithioglycollic	0.86	—	2
Thioglycollic	0.90	—	1
Salicylic	1.00	1	1

It will be noted that the relative adsorption increases with the number of -OH and -COOH groups in the molecule of the acid employed, except in the case of salicylic acid which shows little or no adsorption. The possibility of hydrogen bonding with the cellulose seems strong. The case of salicylic acid can be explained by the internal bonding between the hydrogen of the hydroxyl group and the oxygen of the carboxylic group. This leaves little chance of hydrogen bonding with the cellulose. The figures quoted cannot be taken as quantitative as no values were obtained for the actual concentration of acid in each of the butanol phases employed. The R_F value of each "adsorption front" was measured from the position at which the spots of metallic ions were placed on the paper. The R_F values of the "adsorption fronts" can be taken as relative only when constant conditions of immersion obtain. This point is the subject of further investigation. If the acid is strongly bound to the cellulose, it will not be readily available for complexing with the metal ion. Thus those metals which travel above the "adsorption front" remain as the complex of the anion taken in the original solution, *e.g.* Sn^{IV} travels as the chloride. In some cases, evidence of complexing is manifested. This is indicated by the appearance of two distinct spots, *e.g.*, in the case of Zn^{II} when butanol saturated with 1.0*M* tartaric acid was used as solvent, and also with UO_2^{II} when butanol saturated with 1.0*M* salicylic acid was the solvent employed.

(f) The R_F values obtained with the solvents employed suggest the possibility of the quantitative separation of many cations by selective adsorption or desorption by the application of the descending technique,[6,7].

SUMMARY

Using as solvent, butanol saturated with aqueous solutions of various organic acids, the R_F values of a number of metal ions have been determined by paper partition chromatography. The results obtained may be applied to the qualitative separation of some cation mixtures and the possibility of quantitative separations is indicated in some cases.

RÉSUMÉ

Les valeurs de R_F d'un certain nombre d'ions métalliques ont été déterminées par chromatographie de partage sur papier, en utilisant comme solvant le butanol saturé avec des solutions aqueuses de divers acides organiques. Les résultats obtenus peuvent être appliqués à la séparation qualitative de quelques cations et la possibilité de séparations quantitatives est indiquée dans certains cas.

ZUSAMMENFASSUNG

Die Werte für R_F von einer gewissen Anzahl Metallionen wurden mit Papier-Chromatographie bestimmt. Als Lösungsmittel verwendet man, mit wässrigen Lösungen von verschiedenen organischen Säuren gesättigtes Butanol. Die erhaltenen Resultate können auch für die qualitative Trennung von einigen Kationen angewendet werden und die Möglichkeit von quantitativen Trennungen wird für gewisse Fälle angegeben.

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THE QUANTITATIVE SEPARATION AND DETERMINATION OF TANTALUM AND NIOBIUM USING ANION EXCHANGE CHROMATOGRAPHY

by

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INTRODUCTION

The possibility of using anion exchange for separating niobium and tantalum has been known for some years. KRAUS AND MOORE[1] suggested that anion rather than cation exchange should be particularly useful for separating metal ions which are easily precipitated if not complexed since, under these conditions, cation exchange cannot be used to its full advantage. This applies to elements of the fourth and fifth groups of the periodic table, amongst which are tantalum and niobium.

In a series of papers KRAUS AND MOORE[1,2,3,4] demonstrated that, using mixtures of hydrochloric and hydrofluoric acids and the resin Dowex-1, it was possible to separate tracer quantities of protactinium, niobium, tantalum and zirconium from each other, or one or more of them from any combination of the others. WACKER AND BALDWIN[5] showed that tracer zirconium and niobium could be separated on Dowex-1 using an oxalic acid eluent (tantalum was not investigated) and HUFFMAN, IDDINGS AND LILLY[6] demonstrated a separation of tracer zirconium and hafnium on Dowex-2 using hydrochloric acid as eluent. The latter workers did not attempt a separation of niobium and tantalum, although this appeared to be possible from their data, but stated that the two elements behaved erratically on a column.

The first successful separation of *macro* quantities of niobium and tantalum by anion exchange was by GILLIS, HOSTE, CORNAND AND SPEECKE[7]. Using an oxalic acid eluent 10 mg amounts of the two elements were separated on Dowex-2. A 95% yield of tantalum-free *i.e.* undetectable spectrographically, niobium and an 85-90% yield of tantalum, containing 1% niobium, were obtained. However the method suffered from two disadvantages. Firstly the separation factor for the two elements was small(leading to over-lapping of the two elution curves) and secondly the distribution coefficients of the two elements were large under the conditions used and consequently a large number of free column volumes was needed to elute the two components (something like 40 to 80 for the niobium and 125 to 400 for the tantalum).

The object of the present investigation was to find the most suitable conditions for separating macro quantities of niobium and tantalum by anion exchange using a British resin, Deacidite FF, and a method of applying this separation for analytical use.

Preparation of active niobium and active tantalum

In the preliminary experiments the behaviour of niobium and tantalum was followed by means of the two radionuclides ^{95}Nb and ^{182}Ta. The relationships between these and their parents and daughters are shown in the following series:

$$ {}^{95}_{40}\mathrm{Zr} \xrightarrow[\text{65 day half-life}]{\substack{\text{0.39 MeV } \beta \\ \text{0.73 MeV } \gamma}} {}^{95}_{41}\mathrm{Nb} \xrightarrow[\text{37 day half-life}]{\substack{\text{0.15 MeV } \beta \\ \text{0.76 MeV } \gamma}} {}^{95}_{42}\mathrm{Mo}\text{(stable)} $$

$$ {}^{181}_{73}\mathrm{Ta} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{182}_{73}\mathrm{Ta} \xrightarrow[\text{111 day half-life}]{\substack{\text{0.53 MeV } \beta \\ \text{1.2 MeV } \gamma}} {}^{182}_{74}\mathrm{W}\text{ (stable)} $$

^{95}Nb tracer, separated from fission product ^{95}Zr, is available from the Radiochemical Centre, Amersham. The sample supplied contained a small proportion of longer-lived impurity and was further purifed before use. The solution was made molar in nitric acid and extracted twice with 0.05*M* TTA (thenoyltrifluoracetone) in benzene to remove zirconium. Niobium and zirconium carriers were then added, the solution was evaporated to dryness and the residue was fused with potassium carbonate. The cooled melt was extracted with 2% potassium hydroxide and filtered. Under these conditions the niobium goes into solution but the zirconium does not[8].

After addition of a further quantity of zirconium carrier and another carbonate fusion and removal of zirconium the niobium was finally recovered as niobic acid, dissolved in concentrated hydrochloric acid and stored in 6*N* hydrochloric acid. This stock was used as needed by precipitating the niobic acid with ammonia and dissolving it in the appropriate solvent. The product had the half-life (37 days) and gave β particles of the maximum energy (26-30 mg/cm^2 of aluminium) expected for ^{95}Nb. It contained no detectable impurity.

No difficulty was encountered in preparing radiochemically pure, labelled tantalum; Johnson Matthey's spectrographically pure tantalum pentoxide being irradiated in the Harwell pile (B.E.P.O.) to give 111 day ^{182}Ta. This was normally produced as needed and dissolved by bisulphate fusion, precipitation of tantalic acid and solution in the appropriate solvent.

Distribution coefficient measurements

For the measurement of distribution coefficients (K_D) known weights of resin (usually 1.0 g) were shaken with known volumes (usually 40 ml) of the appropriate solution for at least 48 hours in small polythene phials which were manufactured from tubing and heat-sealed before equilibration. The solutions (except in the case of tungsten) were active and contained the metal under investigation at concentration less than $10^{-3}M$. A portion of the initial solution was retained and a measured volume was counted in a small polythene cup mounted in a gamma scintillation counter. Directly afterwards the same measured volume of the equilibrated solution, separated from resin, was measured in the same cup under the same conditions. The activity before and after equilibration was then compared and the amount of activity absorbed on the resin was obtained by difference.

The resin used for these and the initial column experiments was 'normal' grade Deacidite FF. This was initially converted to the chloride form by the normal procedures, washed and then 'fines' were removed by repeatedly stirring with water and decanting off the suspension. Finally the resin was air dried at room temperature (19°C) and weighed out directly as required.

The distribution coefficient, so determined, is defined by

$$K_D = \frac{\text{Concn. of solute in resin phase}}{\text{Concn. of solute in liquid phase}}$$

$$= \frac{\text{initial activity of solution} - \text{final activity of solution}}{\text{final activity of solution}} \times \frac{\text{volume of solution (ml)}}{\text{mass of resin (g)}}$$

and is approximately related to the elution curve of the solute from an ion exchange column by the equation[9]

$$C = K_D \times \frac{\text{mass of resin in column (g)}}{\text{free column volume (ml)}}$$

where C is the number of free column volumes required to reach the peak of the elution curve of the solute from the point at which eluting solution first reaches the bottom of the column *i.e.* when one free column volume of eluent has passed into the top of the column.

Apparatus for column experiments

The apparatus used for column experiments was of the conventional type except that it was constructed from materials resistant to hydrofluoric acid attack and that no taps were incorporated. In this way the risk of leakage, which is particularly unpleasant when eluents containing hydrofluoric acid are used, was reduced to a minimum. The eluting solution was siphoned from a polythene reservoir through a sufficiently long polythene tube to supply an adequate pressure head (up to 4 feet of water), directly on to the top of the resin in its container which was also made from polythene tubing. A small polythene funnel was sealed on to the end of the column container and this ended in a polythene tube which lead to a fraction collector. The resin was retained in the container by insertion of a pierced polythene disc, or, when very fine resin was used, by a small plug of cotton wool, into the mouth of the funnel. Perspex tubes were used to collect the effluent and these could be changed automatically after collecting for any time period up to 200 minutes each. Flow rate was controlled either by means of screw clips or by the insertion of small capillary tubes, made from pierced polythene rod, in the path of the solution.

In the preliminary experiments active tracers were added and the activity of a measured volume of effluent from each tube was determined by direct gamma counting. The volume of effluent in each tube could then be determined and an elution curve constructed.

Preliminary experiments

Preliminary experiments were carried out to determine the best eluting conditions for separating niobium and tantalum on Deacidite FF. Hydrochloric acid alone was tried first at strengths between $1M$ and $10M$ but it was found that at low concentrations the elements went into colloidal suspension and were immediately eluted from the column whereas at higher concentrations they both adhered too firmly to be removed in a suitably small volume of eluent. Moreover the separation factors *i.e.* the values of $K_{\mathrm{D,Ta}}/K_{\mathrm{D,\ Nb}}$ were not large enough for satisfactory analytical use. The effects of $0.1M$ tartaric and citric acids at pH values between 1 and 8 and in $1M$ to $10M$ HCl was also tried. The addition of either of the two former acids made little or no difference to the behaviour of the two elements which was similar to that observed with hydrochloric acid alone.

In oxalic acid solution, however, the behaviour of niobium is quite different. Wacker and Baldwin[5] found that when niobium is taken up on Dowex-1 from $0.4M$ oxalic acid and eluted with $1M$ hydrochloric-$0.01M$ oxalic acid a normal bell-shaped elution curve was obtained. Gilles *et al.*[7] demonstrated a separation of niobium and tantalum on Dowex-2 by elution with $1M$ hydrochloric-$0.5M$ oxalic acid. The present authors confirmed that both these separations could be achieved when Deacidite FF. was used instead of the Dowex resins. An investigation of the effect of $0.1M$ oxalic acid in hydrochloric acid of strengths between $1M$ and $10M$ showed, however, that the conditions used by Gilles cannot be improved on greatly.

Kraus and Moore[1,3,4] have shown that much larger separation factors can be obtained if hydrochloric-hydrofluoric acid mixtures are used as eluents on Dowex-1. Measurements by the present authors of the distribution coefficients of tantalum and niobium between Deacidite FF and hydrochloric-hydrofluoric acid mixtures (in which the hydrofluoric acid concentration varied from 0.1 to $2.0M$ and the hydrochloric acid concentration from 0.5 to $9.0M$) served to confirm both this and the similarity in behaviour of Dowex-1 and Deacidite FF towards the two elements. It was found that the two conditions required for a good and rapid separation of the two elements, namely a large separation factor and a fairly small distribution coefficient for the element first eluted from the column *i.e.* niobium, occur together when $6M$ hydrochloric—$0.1M$ hydrofluoric or $3M$ hydrochloric—$0.1M$ hydrofluoric acid are used. Moreover in both cases the results are insensitive to quite large increases in hydrofluoric acid concentration (up to $0.25M$).

Of these two possibilities the use of $3M$ hydrochloric —$0.1M$ hydrofluoric acid is to be preferred. It was found that the elution of niobium from identical columns, each 37 cm long, at a linear flow rate of $1.2 \cdot 10^{-3}$ cm/sec resulted in 70 theoretical plates in the case or $3M$ hydrochloric —$0.1M$ hydrofluoric acid and only 23 theoretical plates when $6M$ hydrochloric —$0.1M$ hydrofluoric acid was used as eluent. The number of theoretical plates in each case was determined by means of Glueckauf's formula[10], $N = 8\left(\frac{\overline{v}}{\beta}\right)^2$ where N is the number of theoretical plates obtained, $\overline{v}$ is the volume of solution in ml passed through the column to reach the peak maximum of the elution curve and β is the width of the elution peak in ml measured at a distance 1/e of its height. Since, therefore, $3M$ hydrochloric —$0.1M$ hydrofluoric acid gives sharper peaks it was used for subsequent experiments.

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The behaviour of tantalum and niobium individually could now be examined. A column of Deacidite FF, normal grade, and 44 cm long, was mounted in a polythene tube of diameter 1.35 cm. This was washed for some time with $3M$ hydrochloric—$0.1M$ hydrofluoric acid and then 0.2 mg active niobium was fed to it in a solution of the same composition. The column was eluted with $3M$ hydrochloric—$0.1M$ hydrofluoric acid at a flow rate of 10 ml per hour and the niobium was found to be in the fraction 170 ml to 340 ml from commencement with a peak maximum at 270 ml. The elution curve was of the usual bell-shaped type.

The experiment was then repeated exactly as before but with a feed of 0.3 mg tantalum instead of niobium. On elution the tantalum was found to have moved scarcely at all even though 1350 ml of eluent were passed. The eluent was then changed to $4M$ ammonium chloride—M ammonium fluoride and the tantalum immediately started to move and was recovered in 70 ml of eluate. The use of this latter eluent to remove tantalum was suggested by KRAUS AND MOORE and was found to be ideal for the purpose, but solutions more dilute in either component were found to be quite unsatisfactory.

A separation of macro quantities of the two elements should therefore be possible. Stock solutions of the two elements were made by bisulphate fusion of the spectrographically pure oxides, precipitation of the earth acids with ammonia, collection by centrifuging and solution in $3M$ hydrochloric —$0.1M$ hydrofluoric acid. These stocks were analysed by a method to be given later and weighed quantities (about 10 g of each) were mixed for separation. A 40 cm × 1.43 sq.cm column of normal grade Deacidite FF was used and after the metals had been fed, elution was started with $3M$ hydrochloric —$0.1M$ hydrofluoric acid at a flow rate of 10 ml per hour. The fraction 120 ml to 400 ml from commencement was collected for niobium determination, the

TABLE I

RESULTS OF THE ELUTION SEPARATION OF TANTALUM AND NIOBIUM ON A 40 cm COLUMN OF NORMAL GRADE DEACIDITE FF

Experiment	*Wt Nb_2O_5 taken(mg)*	*Wt Nb_2O_5 found(mg)*	*Nb recovery %*	*Wt Ta_2O_5 taken(mg)*	*Wt Ta_2O_5 found(mg(*	*Ta recovery %*
1	92.3	92.7	100.4 ± 0.4	46.3	42.4	91.6 ± 2.0
2	63.9	63.9	100.0 ± 0.8	68.4	67.4	98.2 ± 0.8

TABLE II

SPECTROGRAPHIC ANALYSES OF Nb_2O_5 AND Ta_2O_5 SEPARATED ON A 40 cm COLUMN OF NORMAL GRADE DEACIDITE FF

Sample	*Result*
1. Nb_2O_5 starting material	Ta_2O_5 content slightly less than spectrographic standard
2. Nb_2O_5 separated from Ta_2O_5 by anion exchange	Ta_2O_5 content undetectable and very much less than spectrographic standard.
3. Ta_2O_5 starting material	Nb_2O_5 content 0.02%
4. Ta_2O_5 separated from Nb_2O_5 by anion exchange	Nb_2O_5 content less than 0.02%

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eluent was then changed to $4M$ ammonium chloride—M ammonium fluoride and the next 60 ml were collected for analysis for tantalum. The recovered oxides were then compared spectrographically with the starting materials. Tables I and II show the results of two such experiments.

The purity of the niobium pentoxide produced was also determined by carrying out another separation from tantalum but this time the tantalum was irradiated in B.E.P.O. to produce 70 μc of activity. The resulting niobium fraction was completely inactive, showing that its tantalum content was certainly less than 0.01% (Johnson Matthey's spectrographically pure niobium pentoxide may contain as much as 1.4% tantalum pentoxide).

The elution of niobium from Deacidite FF

The separations carried out on a 40 cm column took between 40 and 50 hours to effect. For satisfactory analytical use this time must be reduced, and, clearly, this can be done if (1) the column length is reduced and (2) the linear flow-rate is increased. Calculations based on GLEUCKAUF's equations[10] showed that a 12 cm column would be adequate for a complete separation of the two metals using a much faster flow-rate. A column of this length was, therefore, adopted and the effect of increasing flow-rate was examined.

Stock solutions of active niobium and active tantalum were prepared, as described above, from spectrographically pure oxides, to contain 10 mg/ml of either element in $3M$ hydrochloric—$0.1M$ hydrofluoric acid. The experiments were conducted in pairs. First the column (12 cm × 1.27 sq. cm, normal grade Deacidite FF) was fed with 10 ml niobium solution and this was eluted at constant flow-rate and the elution curve was obtained. Next 10 ml niobium solution plus 10 ml tantalum solution were fed, the niobium was eluted at the same flow-rate and its elution curve was again determined. The eluent was then changed to remove the tantalum and the column was regenerated with $3M$ hydrochloric —$0.1M$ hydrofluoric acid. A second pair of experiments was then conducted, identical with the first but with a different flow-rate. In this way the conditions under which tantalum started to come off the column before all the niobium was removed, could be determined.

TABLE III

THE ELUTION OF NIOBIUM BY $3M$ HYDROCHLORIC—$0.1M$ HYDROFLUORIC ACID FROM A 12 cm COLUMN OF NORMAL GRADE DEACIDITE FF AT VARIOUS FLOW RATES

Experiment	1	2	3	4	5
Flow rate (ml/min)	0.355	0.673	1.58	2.75	4.49
Niobium elution begins after (ml)	30	25	20	10	8
Niobium elution is complete after (ml)	205	245	330	370	465
Volume of niobium fraction (ml)	175	220	310	360	457
Niobium peak occurs after (ml)	75	75	76	75	44
Time taken to collect niobium fraction (mins)	577	364	209	135	104

The results are displayed in Table III and show that the elution of niobium is quite normal and similar to the recovery of many cations from cation exchange resins. Up to a flow-rate of 2.75 ml/min no contamination whatever of the niobium fraction by tantalum was observed. At flow rates higher than this traces of tantalum contamination were found, the amount increasing with increasing flow-rate. But even at 4.49 ml/min less than 0.2% of the tantalum appeared in the niobium fraction. At low flow-rates the elution curves are of the usual almost-symmetrical bell-shaped type. As the flow-rate is increased the peak becomes less symmetrical and grows wider and less high *i.e.* the number of theoretical plates is decreased, but the total time taken to collect all the niobium is decreased at the same time. The large volumes which result from rapid recovery of the niobium are inconvenient to handle and can only be reduced, if the column is to be kept a constant length, by using a finer grade resin.

For this purpose normal grade Deacidite FF was air-dried at room temperature, ground in a ball-mill, sieved and the fraction —120 to +200 B.S.S. was separated. This was used in a column

12.3 cm × 1.04 sq.cm and another pair of experiments was carried out with the stock active tantalum and niobium solutions. With a flow-rate of 7.91 ml/min the niobium was collected in the fraction between 30 ml and 180 ml from commencement *i.e.* in 23 minutes, with the peak maximum after 75 ml. There was no interference whatever from the tantalum present.

The elution of tantalum from Deacidite FF

The initial separations of niobium and tantalum (Table I) resulted in poor recoveries of tantalum. To investigate the reason for this the rate of elution at various flow-rates was also studied. A 12 cm × 1.04 sq.cm column of —120 to +200 B.S.S. Deacidite FF was fed with varying amounts of active tantalum in $3M$ hydrochloric—$0.1M$ hydrofluoric acid and after absorption and standing for varying time periods, the tantalum was removed by elution with $4M$ ammonium chloride-M ammonium fluoride. The elution curves were determined and Table IV was constructed from the results.

TABLE IV

THE RATE OF RECOVERY OF TANTALUM FROM A 12 cm COLUMN OF —120 TO +200 B.S.S. DEACIDITE FF BY ELUTION WITH $4M$ AMMONIUM CHLORIDE—M AMMONIUM FLUORIDE

Experiment	1	2	3	4	5*
Amount of tantalum fed to column (mg)	51.3	50.8	51.0	138	49.5
Flow rate (ml/min)	2.08	5.1	8.3	2.03	2.17
% Ta recovered in 25 min		99.04	98.79	95.65	99.45
,, ,, 50 ,,	99.67	99.73	99.65	98.16	99.68
,, ,, 75 ,,		99.85	99.78	99.04	99.77
,, ,, 100 ,,	99.90	99.91	99.85	99.48	99.83
,, ,, 125 ,,		99.96	99.90	99.69	99.87
,, ,, 150 ,,	99.97	99.98	99.94	99.80	99.90
,, ,, 175 ,,		100.00			
,, ,, 200 ,,	100.00		99.99	99.95	99.95
,, ,, 225 ,,			100.00	100.00	
,, ,, 250 ,,					99.99

* In experiments 1 to 4 the tantalum was left on the column for 1 hour before elution. In experiment 5 it was left on for 17 hours before removal.

It will be seen that, when a fixed amount of tantalum is put on the resin, the same time is required on elution to remove any particular fraction of that amount, irrespective of the time it has been allowed to stay on the resin and irrespective of the flow rate used to remove it. If a larger amount of tantalum it put on, however, it requires longer for a fixed fraction to be removed. This behaviour is, of course, quite different from that of niobium (see Table III) where the rate of removal is critically dependent on flow-rate but largely independent of the amount of niobium present.

Whereas niobium is eluted by a process of true ion-exchange it appears that tantalum is removed by simple displacement without re-adsorption. Moreover the very long time required to remove it from the resin suggests that there may be some chemical change necessary (such as the hydrolysis of fluotantalate to oxyfluotantalate) before removal can be effected. This time factor may then be explained by assuming either that the reaction is slow or that the species finally formed diffuses more slowly than the original one through the resin phase.

Irrespective of the actual mechanism of the elution of niobium and tantalum the data given above are sufficient to set the conditions required for a rapid and complete separation of the two elements.

Method for the determination of tantalum and niobium in mixtures of the two

Ion exchange column

Dry some clean chloride-form normal-grade Deacidite FF by exposure to the air, grind in a ball-mill and sieve to obtain a fraction —120 to +200 B.S.S. Make a column, of the type described above, from polythene tubing of cross-section x sq.cm (x must not be less than 1.0), insert a small cotton-wool plug in the bottom and slurry sufficient resin into it with water such that, on settling and gentle tapping, a column of resin 12 cm high is obtained. Wash the resin with several column volumes of $3M$ hydrochloric—$0.1M$ hydrofluoric acid and let the eluent level fall until it is level with the top of the resin.

Preparation of sample solution

The sample, which should not contain more than 100 mg niobium and preferably not more than 50 mg tantalum (although up to 150 mg is permissible), is prepared in 10-15 ml $3M$ hydrochloric —$0.1M$ hydrofluoric acid. If the elements are present as oxides, fuse with bisulphate and crack the melt into 200 ml boiling water in an 800 ml beaker. Boil until the bisulphate has all dissolved (5 to 10 min), cool, adjust the pH to between 6 and 7 with ammonia and digest for a few minutes. Cool to room temperature and centrifuge in a Perspex tube. If the supernate is not completely clear, warm it and filter through an 11 cm Whatman No. 42 paper in a polythene funnel. Wash with a few ml of water and reject the washings.

Add 2 ml $5M$ hydrofluoric acid to the precipitate, or sufficient to dissolve it (if a large amount of tantalum is present a clear solution may not be obtained; this does not matter providing excess hydrofluoric acid is present), then wash the filter paper with 8-10 ml hot $3M$ hydrochloric—$0.1M$ hydrofluoric acid and add this also. Warm if necessary to obtain a clear solution (this may not be possible if a large amount of tantalum is present).

Ion exchange separation

Transfer the solution to the top of the ion exchange column with a polythene dropping tube and allow the liquid level to fall to the top of the resin column at a flow-rate not greater than 3 x ml/min. Begin collecting the effluent immediately in a small graduated cylinder. Wash the Perspex tube out with a few ml $3M$ hydrochloric—$0.1M$ hydrofluoric acid, transfer this to the column and again let the liquid level drop to the top of the resin. Now fill the colum head and begin eluting with $3M$ hydrochloric—$0.1M$ hydrofluoric acid at a flow-rate not exceeding 8 x ml/min.

When 22 x ml *(but not more)* effluent have been collected reject this (as it will contain some potassium salts and impurities) and begin collecting in a graduated polythene vessel. The next 200 x ml will contain all the niobium. Change the collecting vessel and start eluting with $4M$ ammonium chloride—M ammonium fluoride at a flow-rate of 2 x ml/min. If no more than 50 mg tantalum were in the sample it will be removed in 2-2½ hours, but if 50-100 mg were present it will take 2½-3 hours and if 100-150 mg up to 4 hours.

Determination of niobium and tantalum

Transfer the two solutions to large platinum dishes and treat each as follows: — Neutralize with ammonia to the point of incipient precipitation, warm on the hot plate and, when nearly boiling, add a small excess of ammonia. After digesting for a few minutes filter the hot solution through a fluted 15 cm Whatman No. 42 paper, wash with a little water and collect the filtrate and washings in the platinum dish. Boil and add 2g tannic acid, then adjust the pH to 8 with ammonia. Digest for about half an hour, cool, filter through a fluted 15 cm No. 42 paper, add the filter paper containing the earth acid precipitate and ignite both at 850° C to obtain the earth acid oxide.

The reason for this dual precipitation procedure is that the earth acids cannot be completely recovered free from alkali metal salts from fluoride solution by ammonia at pH 8 and the remainders need to be removed as the tannates. On the other hand it is convenient to produce as little tannate as possible not only from the handling point of view but also because impurities have occasionally been found in the tannates when precipitated at this pH.

TABLE V

Experiment	Nb_2O_5 *taken mg*	Nb_2O_5 *found mg*	*Error mg*	Ta_2O_5 *taken mg*	Ta_2O_5 *found mg*	*Error mg*
1	145.1	144.2	—0.9	15.8	17.9	+2.1
2	137.3	137.4	+0.1	121.9	121.9	0.0
3	101.2	101.4	+0.2	162.7	162.8	+0.1
4	101.1	101.5	+0.4	52.6	53.4	+0.8
5	77.7	78.9	+1.2	58.8	59.7	+0.9
6	19.1	19.4	+0.3	116.6	116.1	—0.5
7	17.8	18.2	+0.4	15.4	17.5	+2.1

RESULTS

Using the procedure described above several mixtures of niobia and tantala were analysed; the results are given in Table V. The tantala used was Johnson Matthey's spectrographically pure tantalum pentoxide which contains only about 0.02% niobium pentoxide. The niobium pentoxide used was specially purified by a procedure given elsewhere. It contained less than 5 p.p.m. tantalum pentoxide.

Interfering elements

The scheme described above for the separation of niobium and tantalum allows the first fraction of eluate to be rejected. This removes small amounts of alkali salts which may have been carried through the precipitation stage and which would probably lead to high results when the earth acids were recovered. At the same time it allows any other cationic impurities to be removed. But impurities which are anionic under the elution conditions may be expected to appear in either the niobium or the tantalum fractions. The possible interference of manganese, aluminium, zirconium, iron, titanium, tungsten and tin was examined. Distribution coefficients showed that, of these, manganese and aluminium are not absorbed by the resin at all and zirconium only to a small extent (K_D 0.5) so that none of them are likely to interfere. Iron, titanium and tungsten are absorbed more strongly and may contaminate the niobium fraction whereas tin is retained tenaciously (K_D 274) and will probably come off in the tantalum fraction.

The behaviour of iron, titanium and tungsten was studied under column conditions. 100 mg amounts of radioactive iron and tungsten and inactive titanium were put through the separation procedure. It was found that most of the iron appeared in the first 22 ml of effluent but that 1-2% would appear in the niobium fraction, whereas 97-98% of the titanium and almost 100% of the tungsten would contaminate the niobium fraction.

Since tungsten behaves most like niobium under the elution conditions used an attempt was made to separate niobium and tungsten since, if this separation could be easily accomplished, it may be that the new conditions would also result in a similar separation of niobium from the other elements eluted with it by $3M$ hydrochloric-$0.1M$ hydrofluoric acid.

Distribution coefficients were measured between Deacidite FF and hydrochloric-hydrofluoric acid mixtures (hydrochloric concentration 0.5 to $9M$, hydrofluoric concentration 0.1-$2.0M$) but it was found that the separation factor for tungsten and niobium does not change greatly with variations in composition of the eluent. Consequently it is unlikely that separations of tantalum and niobium under conditions other than those described above would result in much purer products should foreign elements be present.

The most successful eluent for separating tungsten and niobium appeared to be

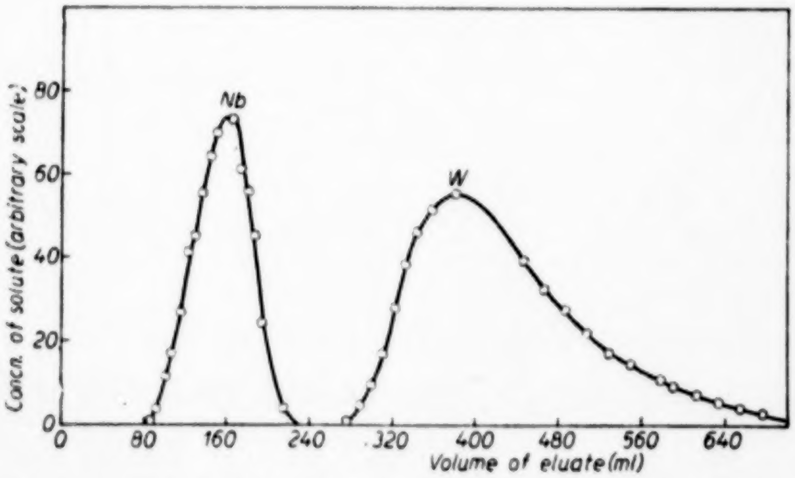

Fig. 1. A separation of tungsten and niobium on Deacidite FF by elution with $9M$ HCl -$0.1M$ HF.

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$9M$ hydrochloric-$0.1M$ hydrofluoric acid. Using this it was found that 100 mg amounts of the two elements could be separated on a 1.27 sq. cm × 22 cm column of —120 to +200 B.S.S. Deacidite FF using a flow-rate of 0.8 ml/min. The elution of the two elements in two distinct peaks is illustrated in Fig. 1.

CONCLUSIONS

The method described provides a simple, accurate, and, considering the difficulty of handling the elements, a fairly rapid method of estimating niobium and tantalum in mixtures of the two. If, however, iron, titanium, tungsten or tin (and possibly some other elements) are present, errors will be introduced unless steps are taken to eliminate their interference.

On modification, the method is readily applied for the production of gram quantities of very pure niobium which contains 5 p.p.m. or less of tantalum pentoxide. As such it has already found use at A.E.R.E., Harwell in the production of reliable spectrographic standards.

The authors are indebted to Mr R. P. THORNE of the Spectrographic Group, A.E.R.E.. Harwell, for the spectrographic analyses reported.

SUMMARY

A method is described for separating and determining niobium and tantalum in mixtures of the two. A solution of the two elements in $3M$ hydrochloric-$0.1M$ hydrofluoric acid is put on a column of Deacidite FF, the niobium is rapidly eluted with $3M$ hydrochloric-$0.1M$ hydrofluoric acid and the tantalum is recovered by elution with $4M$ ammonium chloride-M ammonium fluoride. A complete separation is obtained and the two elements are recovered as their oxides after precipitation. The effects of some other elements have been examined.

RÉSUMÉ

Une méthode est décrite pour la séparation et le dosage du niobium et du tantale. La solution de ces deux éléments dans les acides chlorhydrique $3M$ et fluorhydrique $0.1M$ est passée à travers une colonne de „deacidite FF"; le niobium est rapidement élué par le mélange des acides chlorhydrique $3M$ et fluorhydrique $0.1M$; le tantale est ensuite récupéré par élution avec une solution de chlorure d'ammonium $4M$-fluorure d'ammonium M. Une séparation quantitative est ainsi obtenue et les deux éléments sont précipités comme oxydes. L'influence de quelques autres éléments a été examinée.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben, um das Niobium und das Tantal abzutrennen und zu bestimmen. Die Lösung in Salzsäure $3M$ und in Fluorwasserstoffsäure $0.1M$ dieser beiden Elemente, lässt man durch eine Kolonne von Deacidit FF fliessen. Das Niobium wird rasch durch die Mischung von Salzsäure $3M$ und Fluorwasserstoffsäure $0.1M$ eluiert. Das Tantal wird darauf durch Elution mit einer Ammoniumchlorid $4M$ - Ammoniumfluorid M Lösung zurückgewonnen. Auf diese Weise erhält man eine quantitative Abtrennung und die zwei Elemente werden als Oxyde niedergeschlagen. Der Einfluss von einigen anderen Elementen wurde geprüft.

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USE OF SOME NEW CHELATING AGENTS FOR THE COLORIMETRIC DETERMINATION OF IRON

I. ETHYLENEDIAMINE-BIS-SULPHOSALICYLALDEHYDE

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INTRODUCTION

Numerous organic substances react with ferrous or ferric iron, in solution, to give characteristic colours[1]. The oldest and best known reagent[2], thiocyanate, has been more or less replaced by many of these. The following reagents: 7-iodo-8-hydroxyquinoline-5-sulphonic acid (Loretin or Yatren)[3], *o*-phenanthroline[4], $\beta : \beta' : \beta''$-tetrapyridyl[5] and di-sodium-1 : 2-dihydroxybenzene-3 : 5-disulphonic acid (Tiron or Tifferon)[6] have received considerable attention recently for the spectrophotometric determination of iron.

During the systematic investigation of a series of inner-metallic complex salts of salicylaldehyde and other hydroxyaldehydes with amines, amino-acids and other related compounds, with different metallic ions[7], it was observed that the organic ligand (Schiff's base) formed by the interaction of ethylenediamine and 5-sulphosalicylaldehyde (salicylaldehyde-5-sulphonic acid) gave intense violet-red coloration with ferric iron in solution. This colour intensity is quite high, permitting the detection and estimation of a very small amount of iron. The Schiff's base behaves as a quadridentate ligand, the sulphonic acid group remaining free. The chelate metallic complex formed was isolated in the pure state and its properties were studied.

EXPERIMENTAL

Apparatus. In all the determinations a photoelectric colorimeter (Absorptiometer-Hilger Spekker) was used. Duplicate measurements were also made in a Beckmann Quartz spectrophotometer (D.U. model) using 1 cm correx glass cell. The pH values up to 10 were measured with the glass electrodes using a Cambridge pH meter (Bench type) and the higher pH values were measured with a special alkali electrode.

Solutions. Standard ferric iron solutions were prepared by dissolving E. Merck's (G. R. quality) ferric chloride and ferric nitrate in distilled water, free from traces of iron. Standard solutions of different cations and anions were prepared from C. P. reagents, free from traces of iron.

pH *Adjustments.* The hydrogen ion concentrations of the different solutions were adjusted to a known pH value by using standard solutions of sodium hydroxide, potassium hydroxide, hydrochloric acid and nitric acid.

Reagent[8]. This was prepared by sulphonating pure dry ethylenediamine-bis-salicylaldehyde (Schiff's base) with five times its weight of concentrated sulphuric acid ($d = 1.84$) in a water bath for 2-3 hours, with constant stirring of the mixture. A deep orange-red liquid was obtained. Light yellow crystals of ethylenediamine-bis-salicylaldehyde sulphonic acid separated on cooling the solution in an ice and salt bath. The compound is highly soluble in water and gives a light yellow solution. It is insoluble in alcohol, benzene, acetone, chloroform and dioxane. (Found: C, 44.88; H, 3.89; N, 6.51 and S, 14.96%: $C_{16}H_{14}O_8N_2S_2$ requires C, 44.8; H, 3.73; N, 6.54 and S, 14.95%.)

1-2% of the reagent in distilled water, free from traces of iron, was used. The pH of an 1% solution is about 3.58.

The colour reaction

(i) *Effect of hydrogen ion concentration.* The intensity of the colour was found to vary with the hydrogen ion concentration of the solution. It gives a violet-red coloration instantaneously between pH 1.85 and 7.58. At a higher pH (above 7.6) the colour gradually changes (Fig. 1). It has been noted that the optical density increases up to pH 2.8 and then remains unaltered up to pH 5.7. All measurements were therefore made between the pH values 2.8 and 5.5.

(ii) Maximum absorption (region). The maximum absorption of the colour in the visible region was determined in a Beckmann Quartz Spectrophotometer using a 1 cm corex glass cell (Fig. 2). The maximum absorption of the coloured complex was found to lie between 510 and 520 mμ. Measurements of absorptions were therefore made with a Green (II) filter in the Hilger Spekker Absorptiometer, having a maximum absorption at 520 mμ. The reagent itself showed little absorption in this range.

(iii) *Influence of the reagent.* The reagent itself is slightly coloured (yellow) in aqueous solution but shows negligible absorption at 520 mμ, the wavelength at which the optical density was measured. All measurements were made in the presence of an excess of the reagent. For a solution with a final volume of 50 ml, 10 ml of 1% reagent solution

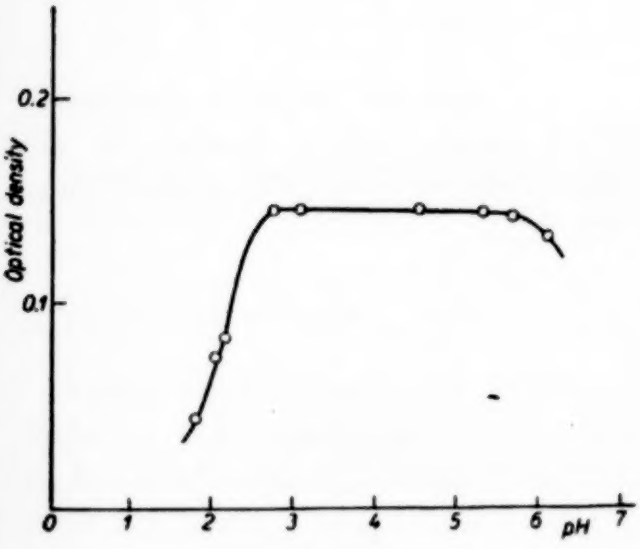

Fig. 1

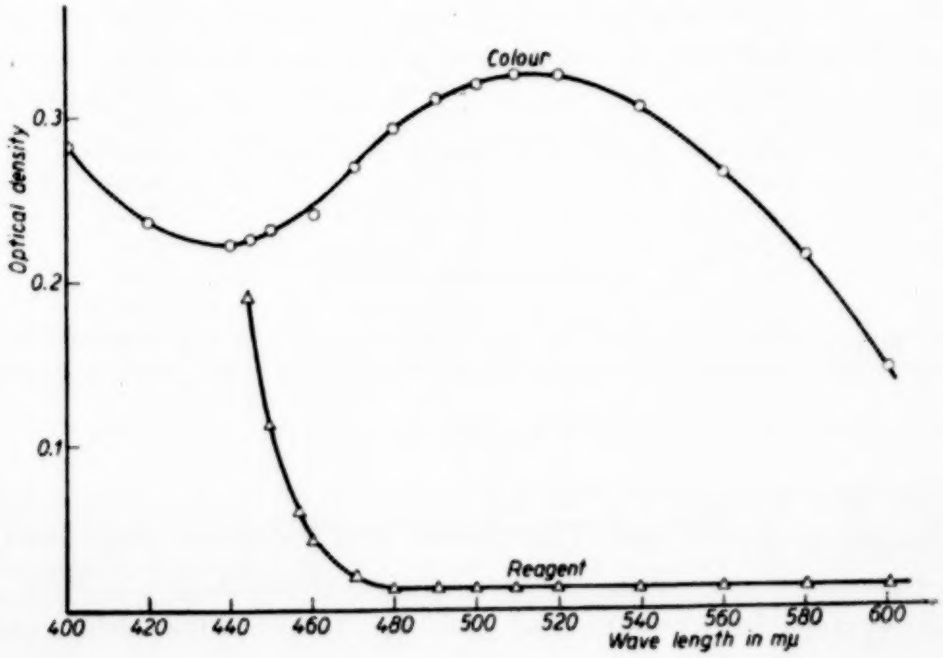

Fig. 2

was sufficient for an iron concentration of up to 5 p.p.m. in the pH range 3.6-4.8. The intensity of the colour formed was not increased by the addition of more reagent.

(iv) *Stability of the colour.* The violet-red colour of the iron complex was quite stable. A solution containing 0.15 mg of iron and 5 ml of reagent at pH 3.6 showed no change in transmittancy even after keeping overnight.

(v) *Influence of temperature.* The optical density of the coloured solution has been found to increase slightly above 40° C and to diminish below 25° C.

TABLE I*

Temperature	*Optical density*
20° C	0.232
25° C	0.240
30° C	0.242
35° C	0.244
40° C	0.248

* Fe = 2 p.p.m. and pH = 4.2 approx.

(vi) *Influence of other ions.* Phosphate, HPO_4^{-2}, borate, BO_3^{-3}, fluoride, F^- and molybdate, MoO_4^{-2} ions have been found to interfere strongly even in very small quantities. The effects of other ions are shown in Table II.

TABLE II

Ion	*Added as*	*Interference* $>$*p.p.m.*
Al^{+3}	$Al(NO_3)_3$	250
Ca^{+2}	$Ca(NO_3)_2$	300
Co^{+2}	$Co(NO_3)_2$	150
Cr^{+3}	$CrCl_3$	100
Cu^{+2}	$CuSO_4$	150
Mg^{+2}	$MgCl_2$	250
Mn^{+2}	$MnCl_2$	180
Ni^{+2}	$NiSO_4$	150
Sn^{+2}	$SnCl_2$	250
Zn^{+2}	$ZnCl_2$	200
ZrO^{+2}	$Zr(NO_3)_4$	250
$HAsO_4^{-2}$	Na_2HAsO_4	200
CH_3COO^-	CH_3COONa	200
$C_2O_4^{-2}$	$Na_2C_2O_4$	80
NO_3^-	KNO_3	200
SO_4^{-2}	Na_2SO_4	150

(vii) *Verification of Beer's law.* The colour was found to obey Beer's law over a wide range of concentration, (Fig. 3). The figure indicates the validity of Beer's law for the coloured system (at 510-520 mμ) over the range from 0.25 to 10 p.p.m.

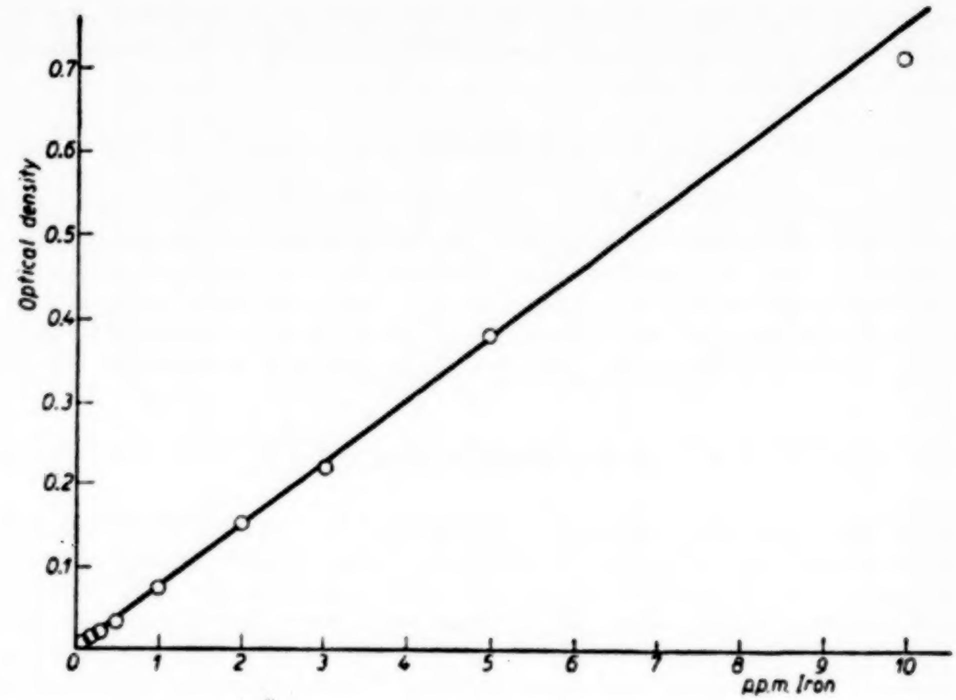

Fig. 3

Sensitivity of colour reactions

Sensitivity measurements were made in photoelectric absorptiometer and the minimum quantity of iron(III) that could be estimated was 0.1 γ per cm^2 (*i.e.* pD = 7).

Metal chelate complex

Ferric-ethylenediamine-bis-sulphosalicylaldehyde chloride was obtained in the pure state by refluxing ferric chloride (1 mol) with ethylenediamine-bis-sulphosalicylaldehyde (Schiff's base) (1 mol) in aqueous alcohol. The mixture was filtered, while hot, after 2-3 hours. The filtrate, on standing over concentrated sulphuric acid in a desiccator, gave violet-red hygroscopic crystals.

The substance is highly soluble in water and pyridine but only sparingly soluble in alcohol and acetone. It is, however, insoluble in chloroform, benzene, ether and toluene. It is decomposed by mineral acid on warming, but is dissolved in dilute alkalis to give a deep-red coloured solution. [Found: Fe, 10.60; N, 5.28; S, 12.14; Cl, 6.68; C, 36.05 and H, 2.93%; $Fe(C_8H_7O_4NS)_2Cl, H_2O$ requires, Fe, 10.44; N, 5.22; S, 11.95; Cl, 6.62; C, 35.84 and H, 2.98%.]

ACKNOWLEDGEMENT

My sincere thanks are due to Professor P. RÂY of the Indian Association for the Cultivation of Science, Calcutta, India, for his helpful suggestions and guidance in the present work.

SUMMARY

Ethylenediamine-bis-sulphosalicylaldehyde, which gives strong violet-red coloration with ferric salts owing to the formation of a stable metal chelate complex, $Fe(C_8H_9O_4NS)Cl.H_2O$, has been utilized for the colorimetric determination of ferric iron, using a Hilger-Spekker photoelectric absorptiometer. The maximum intensity of absorption occurs at pH 2.8-5.5 in the green region (510-520 mμ) of the visible spectrum.

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The colour complex has been found to obey Beer's law between 0.25 and 10 p.p.m. The influences of several foreign ions on the reaction have been carefully studied. The metal chelate complex has been isolated and its properties studied.

RÉSUMÉ

L'éthylènediamine-bis-sulfosalicylaldéhyde, donnant une coloration violet rouge avec les sels ferriques par formation d'un complexe stable $Fe(C_8H_9O_4NS)Cl.H_2O$, a été utilisé pour le dosage colorimétrique du fer(III); on a employé un absorptiomètre photoélectrique Spekker-Hilger. On obtient une intensité d'absorption maximum dans la région du vert (510-520 mμ) aux pH 2.8-5.5. La coloration suit la loi de Beer entre les concentrations 0.25 et 10 p.p.m. L'influence de plusieurs ions étrangers sur la réaction a été examinée. Le chélate formé a été isolé et ses propriétés ont été étudiées.

ZUSAMMENFASSUNG

Das Äthylendiamin-bis-sulfosalicylaldehyd, welches eine rot-violette Färbung mit den Eisen (III) salzen gibt durch Bildung eines stabilen Komplexes $Fe(C_8H_9O_4NS)Cl.H_2O$, wurde für die kolorimetrische Bestimmung von Eisen(III) verwendet. Man gebrauchte ein photoelektrisches Absorptionsmessgerät Spekker-Hilger. Man erhält eine maximale Absorption in der grünen Region (510-520 mμ) bei pH 2.8-5.5. Die Farbintensität folgt zwischen den Konzentrationen 0.25-10 p.p.m. dem Beer'schen Gesetz. Der Einfluss von verschiedenen Fremdionen auf die Reaktion wurde untersucht. Das gebildete Chelat wurde isoliert und seine Eigenschaften studiert.

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USE OF SOME NEW CHELATING AGENTS FOR THE COLORIMETRIC DETERMINATION OF IRON
II. *p*-AMINOSALICYLIC ACID (SODIUM SALT)

by

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INTRODUCTION

Colorimetric reagents for iron are usually divided into two groups, according as they react with ferrous or ferric iron. Many organic substances, especially *o*-hydroxybenzene derivatives and related compounds, react with ferric iron, resulting in the formation of strongly coloured complexes which may be used for the colorimetric estimation of traces of iron.[1] In a previous communication the use of an organic chelating ligand, ethylenediamine-bis-sulphosalicylaldehyde as a new sensitive colorimetric reagent has been reported.[2]

The present paper introduces *p*-aminosalicylic acid (sodium salt), $C_7H_6NO_3Na.2H_2O$, as a new sensitive, stable and widely applicable colorimetric reagent for ferric iron. During the systematic investigation of a series of inner-metallic complex salts[3] of salicylaldimino-acids with metals like copper, nickel, cobalt, manganese, iron and uranium, it was observed that *p*-aminosalicylic acid (sodium salt) reacts with ferrous or ferric iron to give deep violet-red coloration. A careful and systematic study of the reaction of this ligand with ferric iron showed that it is well suited to the colorimetric estimation of the latter. The colour intensity given by the ferric iron in solution is fairly high, permitting detection and estimation of a very small amount of iron(III). The maximum absorption for the colour of the iron complex was found to lie between 480-500 mμ at pH 1.4-3.05, and between 450-470 mμ at pH 3.36-5.05. The colour produced was found to obey Beer's law over a wide range of concentration (0.05 to 15 p.p.m.) and remain stable for a long period of time. The optical density of the coloured solution has been found to diminish slightly below 20° C.

The sodium salt of the *p*-aminosalicylic acid has several advantages over salicylic acid[4] or sulfosalicylic acid. It is highly soluble in water and can be used over a long pH range (between 1.5 and 4.5). The colour of the complex is also stable for a long period of time and is found to obey Beer's law over a wide range of concentration. The coloured product given by *p*-aminosalicylic acid with iron however, could not be isolated in the pure state.

EXPERIMENTAL

Apparatus and solutions. Spectrophotometric determinations were made with a Unicam (SP 600) spectrophotometer using cells of different diameter and in some cases measurements were also made in a photoelectric colorimeter (Absorptiometer-Hilger Spekker type). All pH measurements were made with a Cambridge glass electrode pH meter, (Bench type).

A standard ferric iron solution was prepared from ferric nitrate of reagent quality. The solutions of salts used in studying the effect of various ions in the colour reactions were prepared by dissolving C.P. quality salts in distilled water free from traces of iron.

The pH of the test solutions was adjusted to known desired values using standard solutions of caustic soda, caustic potash, nitric acid or hydrochloric acid.

Reagent. A 1% solution of pure recrystallized sodium salt of the *p*-aminosalicylic acid, $C_7H_6NO_3Na.2H_2O$ was used for the estimation. The sodium salt is stable and highly soluble in the water, while the free acid is only sparingly soluble. The pH of the 1% solution (sodium salt) is about 7.08. (Analysis: N, 6.64%; $C_7H_6NO_3Na.2H_2O$ requires N, 6.63%.)

The colour reaction

(i) *Effect of hydrogen ion concentration.* The intensity of the colour was found to vary with variation of the hydrogen ion concentration of the solution. The nature of the colour was found to vary with pH, red at low pH values (1.44-3.05) and violet-red

TABLE I

pH noted	*Optical density**	
	Blue filter	*Green filter*
1.65	0.420	0.410
1.85	0.462	0.458
2.04	0.612	0.662
2.36	0.614	0.665
2.93	0.660	0.665
3.04	0.678	0.668
3.72	0.718	0.670
4.18	0.704	0.598
4.45	0.675	0.518
5.05	0.608	0.406

* in Hilger-Spekker absorptiometer using 1 cm cell.

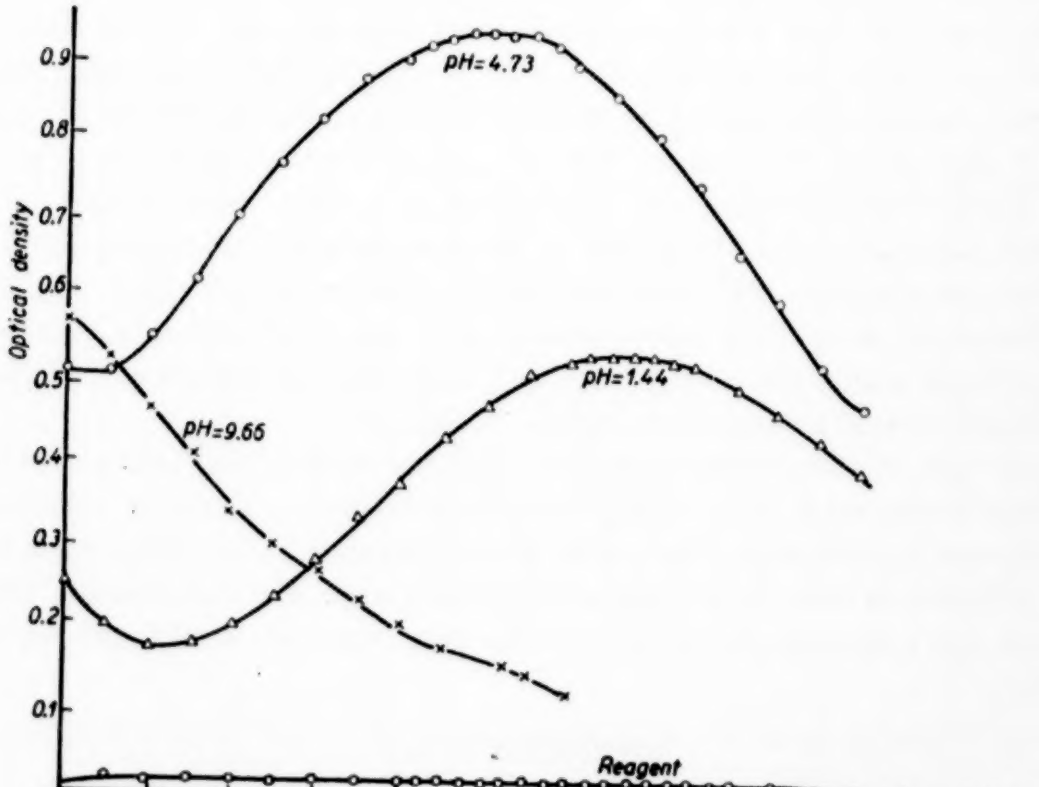

Fig. 1

between 3.35 and 9.86. At lower pH values (below 1.8) the colour fades gradually. The variation of the optical density of the colour system is shown in Table I. It has been noted that the optical density increases slowly with rise of pH; measurements were therefore made at two different values, from 1.8-2.8 and from 3.02-4.55.

(ii) *Maximum absorption (region).* The maximum absorption range of the colour in the visible region was determined in a Unicam (SP 600) spectrophotometer using a 1 cm cell. The maximum absorption of the coloured complex was found to lie between 480 and 500 mμ at pH 1.44 and, between 450 and 470 mμ at pH 4.73. Measurements of absorption were therefore made with a green (Kodak) filter at higher pH values (pH > 3.05) and with a blue (Kodak) filter at low pH values (pH < 2.8) in the Hilger-Spekker photoelectric absorptiometer. The reagent itself showed little absorption in these ranges, (Fig. 1).

(iii) *Influence of the reagent.* The reagent solution is almost colourless and has no influence on the colour of the iron complex. Measurements were always made with a sufficient excess of the reagent (250-50 times). For a solution with a final volume of 25 ml, 5 ml of 1% solution was found sufficient for an iron concentration of 0.00076 g in the pH range 3.85-4.05.

(iv) *Stability of the colour.* Both red and violet-red colours of the iron complex were stable over a long period. A solution containing 0.15 mg of ferric iron and 5 ml reagent at pH 1.68 and 7.06, showed only slight change in transmittancy even on keeping overnight.

(v) *Influence of temperature.* The optical density of the coloured complex has been found to diminish slightly below 25° C. Estimation should therefore be made at temperatures not below 30° C.

(vi) *Influence of foreign ions.* The influence of different ions upon the colour reactions was examined and the results are given in Table II. The reagent gives an intense coloration with uranyl ion, and this therefore interferes with the determination even when present in quantities of 2 p.p.m. Copper, nickel, cobalt, phosphate, borate, fluoride, chromate and molybdate ions have also been found to interfere strongly owing to complex formation.

TABLE II

Ion	*Added as*	*Interference > p.p.m.*
Al^{+3}	$Al(NO_3)_3$	500
Ca^{+2}	$Ca(NO_3)_2$	400
Co^{+2}	$Co(NO_3)_2$	30
Cr^{+3}	$CrCl_3$	80
Cu^{+2}	$CuSO_4$	20
Mg^{+2}	$MgCl_2$	500
Mn^{+2}	$MnCl_2$	400
Ni^{+2}	$NiSO_4$	20
Zn^{+2}	$ZnCl_2$	500
$HAsO_4^{-2}$	Na_2HAsO_4	150
$C_2O_4^{-2}$	$Na_2C_2O_4$	120
CH_3COO^-	CH_3COONa	100
NO_3^-	KNO_3	300
SO_4^{-2}	Na_2SO_4	300

(vii) *Verification of Beer's law.* The colour of the iron complex was found to obey Beer's law over a wide range of concentration, (Fig. 2). The figure indicates the validity

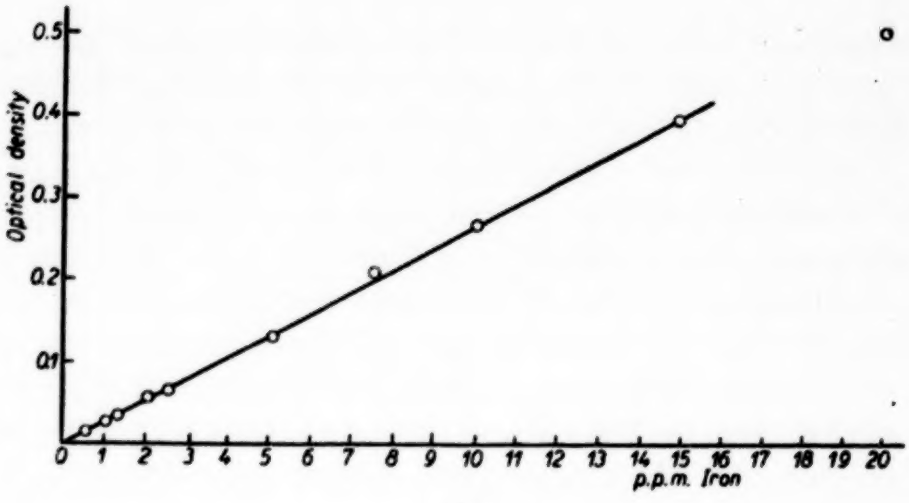

Fig. 2

of Beer's law for the coloured system (at 440-460 mμ) over range from 0.05 to 15 p.p.m. of iron.

Sensitivity of colour reactions

Sensitivity measurement were made in the Unicam spectrophotometer and the minimum quantity of iron(III) that can be determined is 0.05 γ cm^2 (*i.e.*, pD = 7.3).

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My sincere thanks are due to Professor P. RÂY, of the Indian Association for the Cultivation of Science, Calcutta (India) for his kind guidance and helpful suggestions.

SUMMARY

The paper introduces *p*-aminosalicylic acid (sodium salt) as a new, sensitive, stable and widely applicable reagent for the colorimetric determination of ferric iron. The reagent has several advantages over some of the known organic reagents for iron. It can be worked conveniently over a long pH range: 1.5-3.05 or 3.4-5.05. The colour of the complex is also stable for a long period and is found to obey Beer's law over a wide range of concentration.

RÉSUMÉ

Les auteurs proposent l'acide *p*-aminosalicylique (sel de sodium) comme réactif nouveau, sensible et stable pour le dosage colorimétrique du fer(III). Ce réactif peut être utilisé entre les pH 1.5-3.05 ou 3.4-5.05. La coloration du complexe obtenue est stable et obéit à la loi de Beer pour une grande marge de concentrations.

ZUSAMMENFASSUNG

Die Autoren schlagen als neues, empfindliches und beständiges Reaktiv die *p*-Aminosalicylsäure vor (Natriumsalz), um das Eisen (III) kolorimetrisch zu bestimmen. Dieses Reaktiv kann zwischen den pH-Werten 1.5-3.05 oder 3.4-5.05 verwendet werden. Die Farbe des Komplexes ist beständig und gehorcht für eine breite Marge von Konzentrationen dem Gesetz von Beer.

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MICRODOSAGE DU SOUFRE DANS LES MATÉRIAUX BIOLOGIQUES*

par

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Dans une publication de 1954, STRICKLAND et coll.[1] ont décrit une méthode de dosage de la cystéine et de la cystine séparément dans les protéines. Le dernier stade de cette méthode comportait une oxydation du matériel soufré et un dosage du sulfate obtenu. Ce dosage pouvait, d'après les auteurs, être effectué par la gravimétrie classique au baryum. Cependant, la complexité et la concentration saline du milieu au sein duquel on dose le sulfate ne nous ont pas permis d'effectuer des mesures convenables.

Divers autres procédés de dosage ont été essayés:

(1) Précipitation de $BaSO_4$ par un excès connu de sel de baryum, et titrage en retour par complexométrie au versénate de sodium; indicateur: phtaléino-complexon[2]. L'excès de sodium dans le milieu masque le virage de l'indicateur.

(2) Précipitation de $BaSO_4$ par un excès connu de sel de baryum, addition de versénate de magnésium (déplacement du complexe magnésien par le baryum) et titrage complexométrique du magnésium libéré par le versénate de sodium; indicateur: noir ériochrome T[3]. Le virage est très abrupt, mais masqué par l'excès de sels présents.

(3) D'après STRICKLAND[4]: précipitation de $BaSO_4$ par une quantité connue de sel de baryum et titrage en retour par spectrophotométrie de flamme.

(4) Précipitation de $BaSO_4$ par une quantité arbitraire de chromate de baryum en milieu acide, puis passage en milieu alcalin: le $BaCrO_4$ précipite et la quantité de chromate résiduelle est une mesure directe de la quantité de sulfate initialement présente[5] d'après les équations:

pH acide: $x\ SO_4^{-2} + a\ Ba^{+2} \rightarrow x\ BaSO_4 + (a-x)\ Ba^{+2}$

pH alcalin: $(a-x)\ Ba^{+2} + a\ CrO_4^{-2} \rightarrow (a-x)\ BaCrO_4 + x\ CrO_4^{-2}$

Des améliorations de cette méthode ont été introduites qui consistent à précipiter le chromate de baryum en présence d'hydroxyde d'aluminium colloïdal[6], en milieu hydroalcoolique[7] et en utilisant l'ammoniaque comme agent alcalinisant[7] à la place d'hydroxyde de sodium.

C'est ce dernier procédé, notablement modifié, que nous avons utilisé pour le microdosage du soufre.

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PRINCIPE DE LA MÉTHODE

L'échantillon est oxydé dans une bombe à oxygène, de préférence à une bombe au peroxyde, pour éviter l'excès de sels. La réaction est parachevée par ébullition du produit d'oxydation en présence de perhydrol en milieu alcalin.

Le sulfate est précipité, à l'ébullition et en milieu chlorhydrique à pH 0.5 à 1.0 par une quantité déterminée de chlorure de baryum. Dès que la précipitation est amorcée (dix minutes environ après l'addition du chlorure de baryum) le pH est amené vers 3-4 avec de l'ammoniaque. On laisse ensuite reposer la préparation pendant deux heures au moins. La température et le pH initiaux de précipitation ont été choisis en raison de la grosseur des grains, et par conséquent de la solubilité de $BaSO_4$[8]. Le pH final permet une précipitation plus quantitative du sulfate de baryum, sel d'un acide assez faible par sa deuxième acidité ($pK = 1.8$) et par conséquent plus soluble à pH bas. CHARLOT[9] donne pour la solubilité de $BaSO_4$ en milieu HCl les valeurs suivantes:

pH	*Solubilité $BaSO_4$ (mg/100 ml)*	*Solubilité $BaSO_4$ (mg S/100 ml)*
7	0.4	0.13
2	1.0	0.33
0.3	4.7	1.56
0	8.7	2.9

La solution est ensuite traitée par une quantité de chromate de potassium stoechiométriquement équivalente à celle du chlorure de baryum introduite précédemment. Le pH est amené à 9-9.5 avec de l'ammoniaque en milieu hydro-alcoolique, et le chromate de baryum coprécipité avec de l'hydroxyde d'aluminium. On porte à volume et on filtre. On mesure l'extinction du chromate dans le filtrat[7].

PROCÉDÉ

1. Un échantillon titrant 1 à 5 mg de soufre est enroulé dans un petit morceau de papier filtre (S et S 589) que l'on entoure du filament d'allumage. On l'imbibe soigneusement d'éthylène glycol et on verse au fond de la bombe quelques millilitres d'une solution à 5% de carbonate de sodium. Après ignition et refroidissement, on fait barboter l'oxygène dans une solution de carbonate de sodium 5%.
2. Le contenu du flacon laveur est porté à l'ébullition avec 1 ml de perhydrol: le liquide chaud sert à rincer la bombe, et on chauffe la solution avec une nouvelle addition de H_2O_2. L'ébullition est maintenue pendant 15 min pour détruire l'excès d'oxydant.
3. Après refroidissement, on filtre pour éliminer les oxydes et hydroxydes métalliques, les carbonates insolubles et les débris du filament d'ignition. Le résidu est rincé à l'eau.
4. On neutralise le filtrat avec HCl concentré, à chaud, jusqu'à cessation du dégagement de CO_2. Au besoin, on évapore la solution sous une lampe à rayons I.R. pour amener le volume à 80 ml environ.
5. On porte la solution à 100 ml dans un matras. Pour chaque dosage, on prélève une partie aliquote de 10 ml.
6. Dans une petite fiole conique, on introduit 10 ml de la solution à doser, de l'acide chlorhydrique pour amener le pH à 0.5-1.0, et on porte à l'ébullition. Tout en maintenant cette température, on ajoute, goutte à goutte, 5 ml d'une solution de $BaCl_2$ $4.10^{-3}M$. On laisse ensuite refroidir pendant 15 min environ.
7. On élève le pH vers 3-4 avec de l'ammoniaque et on laisse reposer deux heures au moins.
8. Dans un matras de 50 ml, on introduit 5 ml d'une solution de chromate de potassium $4.10^{-3}M$, 2 gouttes d'une solution de chlorure d'aluminium à 10% et 10 ml d'éthanol (exempt d'éther). On y ajoute quantitativement le contenu de la fiole conique, on amène le pH à 9-9.5 avec de l'ammoniaque, et on porte au trait avec de l'eau. On agite et on filtre.
9. On mesure la densité optique du filtrat à 3.700 Å.

RÉSULTATS EXPÉRIMENTAUX

Matériel	*Quantité*	*Teneur théorique* 10^{-6} *Mol. g* SO_4^{-2}	*mg S*	*Teneur mesurée* 10^{-6} *Mol. g* SO_4^{-2}	*mg S*	*Erreur %*	*Moyenne* 10^{-6} *Mol. g* SO_4^{-2}	*Erreur moyenne en %*	*Ecart à la moyenne %*
K_2SO_4 + papier(¹)	1.742 mg	10.0	0.32	10.0	0.32	0	—	—	—
papier(²)	—	0	0	0	0	—	—	—	—
chlorhydrate de cystéine	16.0 mg	101	3.24	97	3.11	4			0.5
				98	3.14	3	97.5	3.5	0.5
,,	10.9 mg	69.4	2.22	69	2.21	0.5			0.5
				69	2.21	0.5			0.5
				68	2.18	1.4	68.5	1	
				68	2.18	1.4			0.4
									0.4
gluten de froment	0.298 g	—	—	281/g	9.01/g	—			0.2
				281/g	9.01/g	—	279/g	—	0.2
				276/g	8.85/g	—			0.3
,,	0.302 g	—	—	284/g	9.10/g	—			0.2
				290/g	9.30/g	—	286/g	—	0.4
				284/g	9.10/g	—			0.2

(¹) Le sulfate de potassium est introduit dans la solution après combustion du papier filtre témoin.
(²) Le papier filtre (S et S 589) mesure 3 × 3 cm².

DISCUSSION

La méthode décrite permet le dosage de quantités de soufre de 1 à 5 mg par échantillon. Cette valeur peut être fortement abaissée en diminuant la quantité de solution de carbonate de sodium utilisée pour retenir les traces de SO_2 qui se trouvent dans l'oxygène. On peut alors réduire le volume final de la solution à doser à 20 ml ou même à 10 ml. La sensibilité de la méthode s'élève alors à 0.1 mg de soufre.

RÉSUMÉ

La méthode mise au point comporte une oxydation totale du matériel soufré en sulfate (à la bombe à oxygène), suivie d'une précipitation au baryum dans les conditions classiques (milieu HCl à l'ébullition). La précipitation est parachevée en amenant le pH à 3-4. Le baryum en excès est précipité, à pH 9, par le chromate, en milieu hydro-alcoolique. Le chromate en excès — représentant le sulfate initial — est dosé colorimétriquement. La précision atteint 2 à 3%. La limite de sensibilité est de 0.1 mg par échantillon.

SUMMARY

The following method is based on the total oxidation, in an oxygen bomb, of the sulphurated matter as sulphate. The latter is precipitated with barium under the classical conditions (boiling HCl-medium) and the precipitation is completed by raising the pH to 3-4 with ammonia. The excess barium is further precipitated as chromate, at pH 9, in an hydro-alcoholic medium and the excess chromate — stoechiometrically equivalent to the initial sulphate — is colorimetrically determined. The smallest amount of sulphur that can be determined is 0.1 mg per sample. Accuracy is about 2-3%.

ZUSAMMENFASSUNG

Die ausgearbeitete Methode besteht in einer vollständigen Oxydation des schwefelhaltigen Materials, zu Sulfat (mit Hilfe einer Sauerstoffbombe), welche einer Ausfällung mit Barium unter den klassischen Bedingungen vorangeht (in HCl bei Siedetemperatur).

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Die Ausfällung wird vollends beendigt, indem man den pH auf 3-4 bringt. Der Überschuss an Barium wird bei pH 9 mit Chromat in einem Wasser-Alkoholgemisch ausgefällt. Der Überschuss an Chromat, welcher das anfängliche Sulfat repräsentiert, wird kolorimetrisch bestimmt. Die Präzision erreicht 2-3%. Die Sensibilitätsgrenze ist 0.1 mg pro Substanzentnahme.

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COULOMETRIC DETERMINATION OF NICKEL AND COBALT

by

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Nickel and cobalt have very similar electrochemical characteristics, and no satisfactory method has previously been described for their electrolytic separation by reduction to the metallic state. BALACHOWSKY[1] attempted the deposition of nickel on a platinum cathode in the presence of cobalt from a buffered thiocyanate solution but the results were far from satisfactory. The usual electrolytic method for separating the two elements, originated by COEHN AND GLÄSER[2] and improved by TORRANCE[8], involves anodic deposition of the cobalt as cobaltic oxide. However, the latter is invariably contaminated with nickel, and in accurate work the first deposit must be dissolved and the separation repeated. The variable composition of the cobaltic oxide deposit precludes direct weighing, so that the second deposit must be dissolved and the cobalt finally deposited as the metal. More recently NENADKEVICH[7] reported the electrolytic separation of nickel and cobalt from an alkaline cyanide solution. Nickelic oxide deposits on the platinum anode and the cobalt is held in solution as cobalticyanide ion. As with cobaltic oxide the composition of the nickelic oxide deposit is variable, so that it must be dissolved and its nickel content determined by one of the standard methods.

The fact that in thiocyanate or pyridine media +2 nickel and +2 cobalt yield well separated polarographic waves for reduction to the metals[5] prompted this investigation of their separation and coulometric determination on the macro scale by controlled potential electrolysis with a mercury cathode using an aqueous pyridine electrolyte.

EXPERIMENTAL TECHNIQUE

The electrolysis cell (100 ml capacity and mercury cathode area of 20 cm^2) was the same as that described by LINGANE[4]. A constant speed (600 r.p.m.) mechanical stirrer was used, with the stirring blades adjusted to keep the mercury-solution interface in rapid but smooth motion. The cell was closed with a Bakelite cover, and dissolved oxygen was removed from the solution with a stream of nitrogen.

Two types of anode, immersed directly in the test solution, were used; a silver anode with either chloride or bromide as depolarizer, and a platinum anode with hydrazine as depolarizer[4]. The silver anode (area 103 cm^2) was essentially the same as in previous studies[4]. The platinum anode (area 75 cm^2) was a gauze cylinder, mounted vertically and coaxially with the stirrer shaft.

A potentiostat[4] was used to maintain automatically the potential of the mercury cathode at a constant value against a saturated calomel reference electrode.

The quantity of electricity passed was measured with a hydrogen-oxygen coulometer[4] when the initial current was larger than about 30 milliamp. With smaller initial currents it was found that the hydrogen-oxygen coulometer was subject to a significant negative error. Therefore, when small quantities (less than *ca.* 20 mg) of metal were determined the quantity of electricity passed was measured with a gravimetric silver coulometer. The electromechanical integrator described by LINGANE AND JONES[6] may be used, and it is more convenient than either the gas or silver coulometers.

The technique of the determinations was as follows. The supporting electrolyte alone was placed in the cell, dissolved air was removed with purified nitrogen, and the solution was subjected to a preliminary electrolysis with the potential of the mercury cathode at —1.20 V *vs.* S.C.E. to remove traces of reducible impurities. The preliminary electrolysis was continued until the background current decreased to a constant minimal value, which usually required 30 to 60 minutes. The potentiostat was then set to maintain the potential of the cathode at the value to be used in the determination (—0.95 V *vs.* S.C.E. for nickel and —1.20 V for cobalt), the sample solution was added, and electrolysis was allowed to proceed under automatic control until the current decreased to a constant minimal value. The total quantity of electricity passed, the electrolysis time, and the final current were noted.

Correction for the quantity of electricity associated with the background current was applied by subtracting the product of the final current (amperes) and the electrolysis time (sec) from the total number of coulombs indicated by the coulometer. The background current probably results from reduction of hydrogen ion, and this method of correction assumes that it is constant throughout the electrolysis.

The quantity of metal deposited W was calculated from the relation

$$W = \frac{M(Q - i_b t)}{2F}$$

where M is the atomic weight, Q the total quantity of electricity (coulombs) indicated by the coulometer, i_b the final background current (amp), t the electrolysis time (sec), and F is the faraday.

Standard solutions of nickelous chloride and cobaltous chloride were prepared from the purest commercially available salts. The nickel solution was standardized by the dimethylglyoxime method, and the cobalt solution by oxidation to cobaltic oxide with hydrogen peroxide in alkaline medium and iodometric assay of the +3 cobalt. The significant amounts of nickel impurity in the cobalt salt and cobalt impurity in the nickel salt were determined by polarographic methods,[3,5] and the appropriate corrections were applied.

The pyridine used (Mallinckrodt Analytical Reagent) was redistilled, and the middle fraction boiling within a 2° range was collected.

RESULTS AND DISCUSSION

The optimum control potentials for the deposition and separation of nickel and cobalt were established by determining the deposition potentials polarographically with the dropping mercury electrode. Polarograms were recorded in the usual manner with a polarograph at a relatively low sensitivity, and the deposition potential was measured by extrapolating the nearly linear steeply rising part of the c.v. curve back to intersection with the residual current.

The deposition potentials (at a metal ion concentration of *ca.* $0.02M$) were determined over a wide range of pH in an electrolyte containing $1M$ total pyridine and $0.5M$ chloride ion (added as either hydrochloric acid or potassium chloride). The potentials at which reduction of the supporting electrolyte occurred were also determined.

As shown in Fig. 1, the deposition potentials of both metals are practically constant over the pH range from 4 to 9. In neither case does the reduction of the pyridine-metal ion complex proceed reversibly; if it did the deposition potential would shift to a more negative value with increasing pH because of the increasing concentration of free pyridine. At a pH below about 4 complexation with pyridine is prevented by the conversion of the latter to pyridinium ion (pK_a for pyridinium ion is 5.4). The abrupt negative shift of the deposition potential of cobalt at pH = 3.5 is simply a manifestation of the well known fact that the overpotential required for the discharge of aquo cobaltous ion is larger than that for the cobaltous-pyridine complex.

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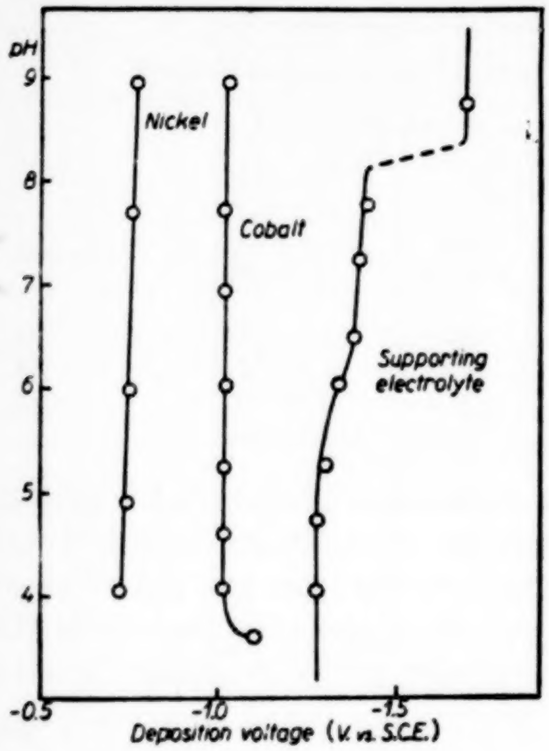

Fig. 1. Deposition potentials of nickel and cobalt at a mercury cathode from aqueous pyridine medium as a function of pH.

From these data a potential of —0.95 V *vs.* S.C.E. was selected as optimum for the separation of nickel from cobalt over the entire pH range. A potential of —1.20 V is satisfactory for the deposition of cobalt without interference from reduction of the supporting electrolyte.

Results with silver-silver chloride auxiliary anode

Typical performance data obtained with the silver-silver chloride auxiliary electrode are shown in Tables I and II. Exactly similar data were obtained in a series of experiments with a silver-silver bromide auxiliary electrode, and in another series using a divided cell like that on p. 371 of Reference 4.

The chief factor limiting the precision of these determinations, and the smallest quantity of the metals it is feasible to determine, is the appreciable background current

TABLE I

SEPARATE DETERMINATIONS OF NICKEL AND COBALT WITH SILVER-SILVER CHLORIDE ANODE

Electrolyte 1.00*M* total pyridine, 0.50*M* chloride. Volume *ca.* 100 ml

Nickel at —0.95 V vs. S.C.E.

pH	*Nickel taken mg*	*Initial current mA*	*Residual current mA*	*Time min*	*Total coulombs*	*Nickel found mg*	*Error mg*
5.3	208.6	250	4.2	165	723.9	207.5	—1.1
5.3	104.3	140	1.8	150	359.8	104.5	0.2
5.3	104.3	175	2.7	150	368.1	104.6	0.3
5.3	104.3	160	3.8	162	383.6	105.4	1.1
5.3	20.9	66	2.7	105	86.4	21.1	0.2
5.3	20.9	67	1.6	120	78.0	20.2	—0.7
6.6	104.3	250	2.6	150	367.2	104.6	0.3
7.9	104.3	230	1.5	120	354.4	104.5	0.2
9.0	104.3	140	2.2	120	358.1	104.1	—0.2
9.3	104.3	148	4.3	157	386.3	105.2	0.9
						Av.	±0.5

Cobalt at —1.20 V vs. S.C.E.

pH	*Cobalt taken mg*	*Initial current mA*	*Residual current mA*	*Time min*	*Total coulombs*	*Cobalt found mg*	*Error mg*
5.3	102.9	130	2.8	174	440.7	125.7	22.8
5.3	102.9	170	2.8	120	387.0	112.0	9.1
5.4	102.9	170	2.2	150	395.9	114.9	12.0
6.4	102.9	220	2.5	150	359.7	103.0	0.1
7.4	102.9	230	1.7	180	355.0	102.8	—0.1
9.2	102.9	230	2.8	120	356.1	102.6	—0.3
9.2	51.5	175	3.9	120	198.6	52.1	0.6
9.2	20.6	83	2.4	120	87.0	21.3	0.7
						Av. (above pH 6.4)	±0.4

TABLE II

ANALYSIS OF NICKEL-COBALT MIXTURES WITH SILVER-SILVER CHLORIDE ANODE

Electrolyte 1.00*M* total pyridine, 0.50*M* chloride
Electrolysis at −0.95 V *vs.* S.C.E. for nickel and at
−1.20 V *vs.* S.C.E. for cobalt

	pH	*Nickel taken mg*	*Nickel found mg*	*Error mg*	*Cobalt taken mg*	*Cobalt found mg*	*Error mg*
1	9.0	104.6	105.3	0.7	103.3	103.1	−0.2
2	9.1	104.6	105.2	0.6	103.3	103.7	0.4
3	9.0	104.6	104.3	−0.3	103.3	104.2	0.9

due to reduction of the supporting electrolyte. From experiments in which the gain in weight of the silver anode was compared with the quantity of electricity passed, it was established that about one-half the background current results from the reduction of the constant small concentration of dissolved silver present in the solutions. From the known polarographic behavior of pyridine,[3] the remainder probably results from a catalyzed reduction of hydrogen ion at pH values below about 6 and from reduction of pyridine at higher pH's.

As explained above, correction for the background current was applied by assuming that the background current during the entire electrolysis was the same as the final residual current; *i.e.*, that the background current was not influenced by the metal deposition. The results in Table I demonstrate that this assumption is valid in the case of nickel over the entire pH range, but with cobalt it is valid only when the pH is greater than about 6. At pH values less than 6 the background current while cobalt is being deposited evidently is considerably greater than at the end of the electrolysis. Cobalt is insoluble in mercury, and apparently the hydrogen overpotential on the freshly deposited metal is significantly smaller than after the metal deposit has aged.

Platinum auxiliary anode with hydrazine as depolarizer

The use of a platium auxiliary anode depolarized by hydrazine is somewhat more convenient than a silver-silver chloride anode[4]. More importantly the background current with the platinum-hydrazine anode is only about half as large as with the silver-silver chloride anode. A further incidental advantage is that the nitrogen produced by the oxidation of the hydrazine, according to $N_2H_4 = N_2 + 4H^+ + 4e$, aids in excluding air from the solution.

Since it was expected that hydrazine might form complexes with nickel and cobalt which could change their deposition characteristics, a polarographic investigation of nickel and cobalt in the presence of hydrazine, both with and without pyridine present, was carried out. This showed that above a pH of about 6 both metals do form complexes with hydrazine, whose deposition potentials are about 0.2 V more negative than the pyridine complexes. In the presence of both pyridine and hydrazine both complexes co-exist over the pH range from about 6 to 8, and the polarogram shows a separate wave for each.

This is demonstrated in the case of nickel by the typical polarograms in Fig. 2. The single wave at pH = 5.3 results from reduction of the nickel pyridine complex, while the single wave at pH = 8.5 is that of the nickel hydrazine complex. At intermediate pH values a doublet wave is observed, the first wave being that of the nickel

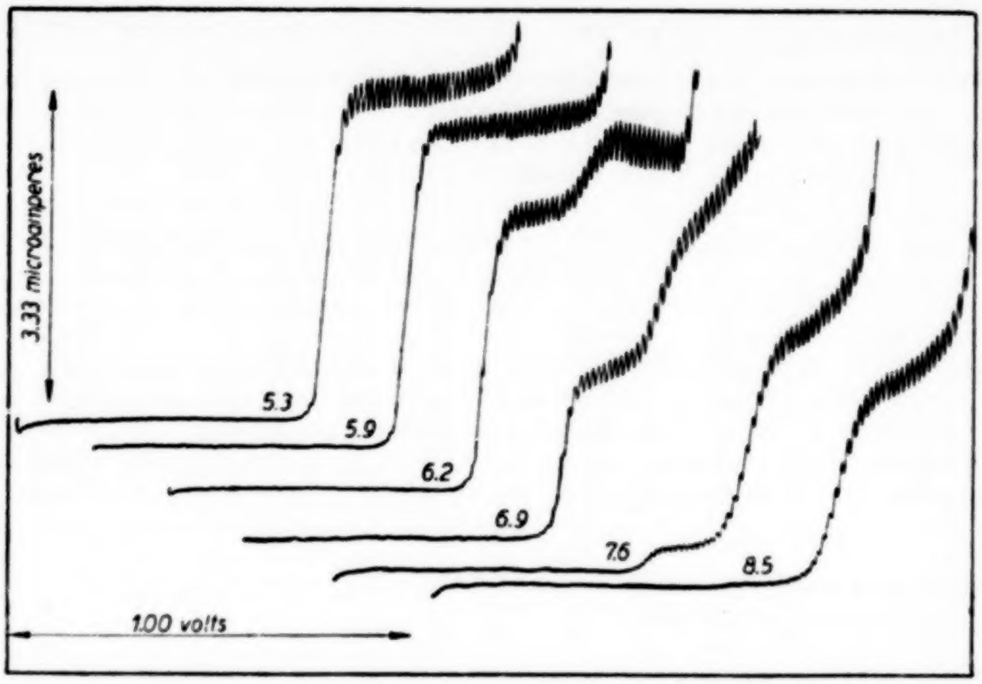

Fig. 2. Polarograms of nickel in the simultaneous presence of pyridine (1M) and hydrazine (0.2M) at the pH values indicated for each curve. Each curve starts at 0 V *versus* the saturated calomel electrode. The galvanometer zero was displaced downward for each successive curve to avoid overlapping.

pyridine complex. The occurrence of the doublet wave shows that the rate of transformation of the hydrazine complex to the pyridine complex is relatively slow.

Some transformation (albeit incomplete during the life of a mercury drop at the dropping electrode) does take place at potentials at which the pyridine complex is reduced. Consequently the ratio of the pyridine and hydrazine complexes in the body of the solution doubtless is somewhat smaller than the relative heights of the two waves.

At pH values below 7.5 both metals can be deposited from the mixed pyridine-hydrazine solution at the same potentials used in the absence of hydrazine, because the hydrazine complexes are transformed to the pyridine complexes as the deposition of the latter proceeds. However, at a pH above 7.5 this transformation is so slow that an inordinately long time is required for complete deposition.

With the pyridine-hydrazine electrolyte nickel can be determined satisfactorily over the pH range from 5.2 to 7.2. However, for determination of cobalt the pH must be above about 6.3 to prevent the catalyzed reduction of hydrogen ion described above. Consequently for the successive determinations of both metals the pH must be between about 6.3 and 7.2. Because the hydrogen ion produced by the oxidation of hydrazine at the anode causes a significant decrease in pH the optimum initial pH is 7.0±0.2 when the supporting electrolyte contains 1M total pyridine and 0.2M hydrazine. With up to 100 mg of cobalt in 100 ml the concentration of hydrazine should not be much smaller than 0.2M. With only 0.1M hydrazine a few tenths of a milligram of cobaltic oxide was observed to deposit on the platinum anode, but this does not occur with 0.2M hydrazine.

The data in Table III show that the successive determinations of nickel and cobalt are very satisfactory under the optimum conditions.

Because the deposition of each metal requires 2 to 3 hours the total elapsed time for a successive determination of both is 4 to 6 hours. However, since the electrolyses are automatically controlled by the potentiostat, the actual operator time involved is

TABLE III

SEPARATION OF NICKEL AND COBALT, PLATINUM-HYDRAZINE ANODE

Electrolyte 1.00M total pyridine, 0.30M chloride, and 0.20M hydrazine sulfate.
Electrolysis at —0.95 V *vs.* S.C.E. for nickel and at —1.20 V for cobalt.

	pH	*Nickel taken mg*	*Nickel found mg*	*Error mg*	*Cobalt taken mg*	*Cobalt found mg*	*Error mg*
1	7.0-6.6	104.6	104.8	0.2	103.3	103.0	—0.3
2	6.7-6.1	104.6	105.1	0.5	103.3	a	
3	7.1-6.8	87.0	86.5	—0.5	17.7	18.5	0.8
4	7.0-6.7	87.0	86.5	—0.5	17.7	1.80	0.3
5	7.0-6.6	17.6	17.7	0.1	85.6	85.5	—0.1
6	7.1-6.6	17.6	18.3	0.7	85.6	85.3	—0.3
			Av.	±0.4		Av.	±0.4

a) Final pH too low for cobalt detn.

only that required to reset the potentiostat and observe the coulometer readings. Once the test solution has been prepared the operator time need not exceed about twenty minutes. This is less than the actual operator time required to analyse a mixed nickel-cobalt solution with equal accuracy by any of the classical methods.

Commercial nickel salts invariably contain significant amounts of cobalt, and the converse is true of cobalt compounds. Ordinary purification techniques are not very effective in removing small amounts of cobalt from nickel salts, and *vice versa*. Since the controlled potential technique described herein provides a very clean separation of nickel from cobalt, it can be used very advantageously for preparing nickel-free cobalt compounds and cobalt-free nickel compounds.

ACKNOWLEDGEMENTS

Grateful acknowledgement is made to the Mallinckrodt Chemical Works for partial financial support of this investigation, and to the Research Council of Ontario for scholarship aid to the junior author.

SUMMARY

A method has been developed for the successive determinations of nickel and cobalt by controlled potential coulometric analysis with a mercury cathode, using an aqueous pyridine electrolyte. Quantities of the metals from about 10 to 100 mg per 100 ml are determinable with an average error of ±0.5 mg. Because this controlled potential electrolysis technique produces a clean separation of nickel and cobalt it can be used for preparing nickel-free cobalt compounds and cobalt-free nickel compounds.

RÉSUMÉ

Une méthode a été mise au point pour doser successivement le nickel et le cobalt par analyse coulométrique à potentiel contrôlé, en solution eau-pyridine, en utilisant une cathode de mercure. Des quantités de ces métaux d'environ 10 à 100 mg/100 ml peuvent être déterminées avec une erreur moyenne de ± 0.5 mg. Grâce à l'excellente séparation nickel-cobalt, obtenue par cette électrolyse à potentiel contrôlé, cette technique peut être utilisée pour la préparation de composés de nickel exempts de cobalt et de composés de cobalt exempts de nickel.

ZUSAMMENFASSUNG

Es wurde eine Methode ausgearbeitet, um Nickel und Kobalt mit einer coulometrischen Analyse bei kontrolliertem Potential in einer Wasser-Pyridin Lösung nacheinander zu bestimmen, unter

Verwendung einer Quecksilberelektrode. Mengen dieser Metalle von 10 bis 100 mg/100 ml können mit einem mittleren Fehler von ± 0.5 mg bestimmt werden. Dank der hervorragenden Trennung von Nickel-Kobalt, welche man mit dieser Elektrolyse bei einem kontrollierten Potential erhält, kann diese Technik auch für die Präparation von Nickel-Verbindungen, welche kein Kobalt enthalten, und von Kobalt-Verbindungen, welche kein Nickel enthalten, verwendet werden.

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POTENTIOMETRIC STUDIES IN OXIDATION-REDUCTION REACTIONS

XX. REDUCTION WITH FERROUS ETHYLENEDIAMINE SULPHATE INDIRECT DETERMINATIONS

by

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CARAWAY AND OESPER[1] have prepared ferrous ethylenediamine sulphate, $FeSO_4.(CH_2.NH_3)_2SO_4.4H_2O$, and showed that it reacted stoichiometrically with standard solutions of three powerful oxidizing agents, namely, potassium dichromate, potassium permanganate and ceric sulphate which are commonly employed in oxidimetric titrations.

In acid medium ferrous ethylenediamine sulphate reacts with potassium permanganate, hydrogen peroxide, potassium persulphate, potassium dichromate, potassium chlorate, potassium bromate and ceric sulphate[2].

EXPERIMENTAL

A known weight of each substance was mixed with an excess of standard ferrous ethylenediamine sulphate solution and the mixture acidified with sulphuric acid. Phosphoric acid mixture was used in the case of potassium persulphate, potassium chlorate and potassium bromate. 5 to 10 ml of Zimmermann's reagent were also added when the mixture contained potassium chlorate or potassium bromate. The mixture containing potassium chlorate was heated for about ten minutes to 80° C

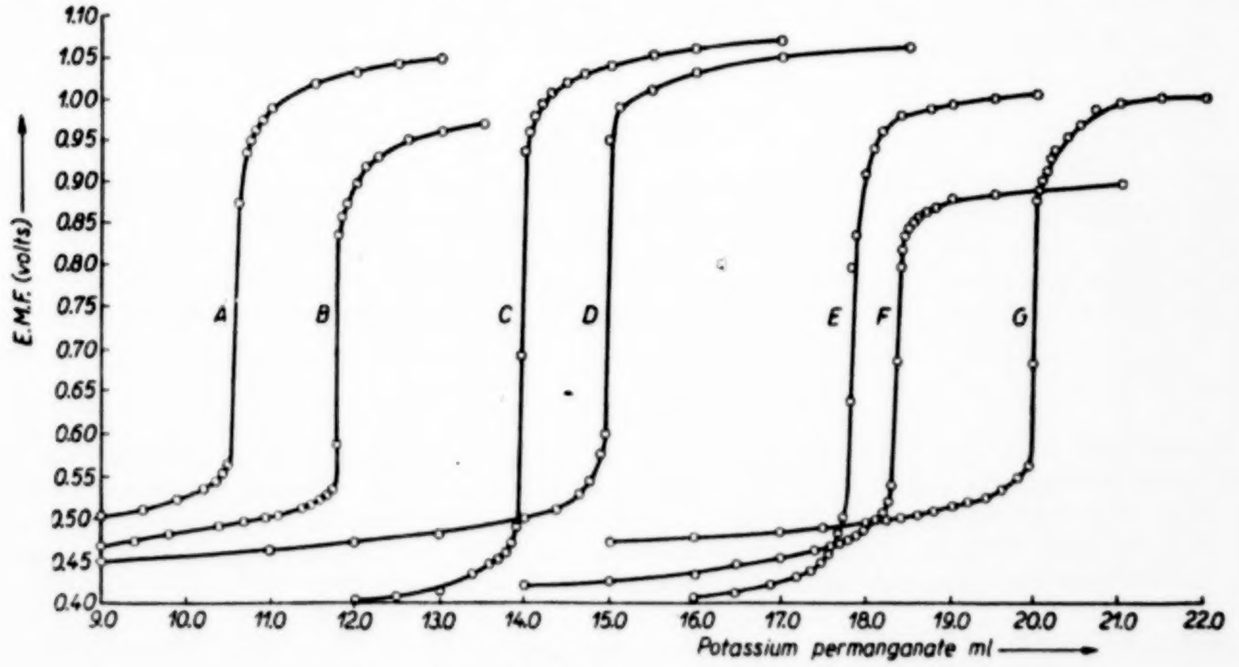

Fig. 1. Curves A $KMnO_4$ E $KClO_3$
B H_2O_2 F $KBrO_3$
C $K_2S_2O_8$ G $Ce(SO_4)_2$
D $K_2Cr_2O_7$

TABLE I

Titration of 0.01235 g of potassium dichromate mixed with 5 ml of water, 20 ml of 0.05*N* ferrous ethylenediamine sulphate and 20 ml of 4*N* H_2SO_4, against 0.05*N* potassium permanganate solution.

Potassium Permanganate ml	*E.M.F. (volts)*	*E/C (mvolts/ml)*
0.00	0.3992	
		4
1.00	0.4031	
		5
3.00	0.4137	
		5
6.00	0.4301	
		6
9.00	0.4469	
		7
11.00	0.4610	
		9
12.00	0.4704	
		11
13.00	0.4815	
		19
14.00	0.5007	
		33
14.40	0.5138	
		53
14.70	0.5300	
		115
14.80	0.5415	
		280
14.90	0.5695	
		652
14.95	0.6021	
		7026 (maximum)
15.00	0.9534	
		312
15.05	0.9690	
		226
15.10	0.9803	
		93
15.20	0.9896	
		83
15.50	1.0144	
		32
16.00	1.0305	
		19
17.00	1.0495	
		10
19.00	1.0687	
		5
22.00	1.0830	
		3
25.00	1.0920	

in an atmosphere of carbon dioxide and then allowed to cool. In each case the excess ferrous ethylenediamine sulphate was titrated at 20° C against standard potassium permanganate solution by a potentiometric method. The mixture was kept stirred by a mechanical stirrer during the titrations. A bright platinum foil immersed in the solution to be titrated was used as an oxidation-reduction electrode, and this was coupled with a saturated calomel electrode through an agar-agar potassium chloride bridge. During the titration the progress of the reaction was studied potentiometrically. At the equivalence point a sharp jump in potential was observed in each titration.

A series of potentiometric titrations were performed with different amounts of each substance. One titration, as typical of the set, is recorded in Table I.

All chemicals, except ceric sulphate, used in this investigation are of guaranteed purity. Ceric sulphate was standardized with pure arsenious oxide[3]. Acid normality of the mixture was kept between 1 and $2N$ in the potentiometric titrations.

Phosphoric acid mixture was prepared by mixing 75 ml H_2SO_4 (Sp. gr. 1.84) with 75 ml H_3PO_4 (Sp. gr. 1.75) and diluting it to 500 ml with distilled water.

The titrations, one for each substance, are represented by the curves, A to G, given in Fig. 1.

In these titrations it is evident that with the addition of the titrant the E.M.F. rose steadily till the equivalence point. At the equivalence point there was a sharp jump in potential followed by a steady rise in each case.

From the amount of potassium permanganate used, corresponding to the equivalence point in each titration, the amount of ferrous ethylenediamine sulphate required for the reduction of each substance was calculated and consequently the amount of each substance was determined. The results recorded in Tables II—VIII show that potassium dichromate, potassium permanganate, hydrogen peroxide, potassium persulphate, potassium chlorate, potassium bromate and ceric sulphate can be determined indirectly by the potentiometric method, using ferrous ethylenediamine sulphate (FES) as a reducing agent.

TABLE II

POTASSIUM DICHROMATE

$K_2Cr_2O_7$ taken g	$N/20$ FES added ml	$N/20$ $KMnO_4$ used for excess FES ml	$N/20$ FES used by $K_2Cr_2O_7$ ml	$K_2Cr_2O_7$ found g
0.0123	20.00	14.960	5.040	0.0123
0.0243	20.00	10.036	9.964	0.0243
0.0343	20.00	5.992	14.008	0.0342
0.0441	37.00	18.981	18.019	0.0440
0.0590	48.00	23.918	24.082	0.0587

TABLE III

POTASSIUM PERMANGANATE

$KMnO_4$ taken g	$N/20$ FES added ml	$N/20$ $KMnO_4$ used for excess FES ml	$N/20$ FES used by $KMnO_4$ ml	$KMnO_4$ found g
0.0088	25.00	19.459	5.541	0.0088
0.0133	25.00	16.555	8.445	0.0134
0.0190	25.00	12.969	12.031	0.0190
0.0229	25.00	10.512	14.488	0.0229
0.0276	25.00	7.541	17.459	0.0276

TABLE IV

HYDROGEN PEROXIDE

H_2O_2 taken g	$N/20$ FES added ml	$N/20$ $KMnO_4$ used for excess FES ml	$N/20$ FES used by H_2O_2 ml	H_2O_2 found g
0.0041	25.00	20.240	4.760	0.0041
0.0047	25.00	19.312	5.688	0.0048
0.0088	25.00	14.689	10.311	0.0088
0.0113	25.00	11.761	13.239	0.0113
0.0152	25.00	7.140	17.860	0.0152

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TABLE V

POTASSIUM PERSULPHATE

$K_2S_2O_8$ found g	*N/20 FES added ml*	*N/20 $KMnO_4$ used for excess FES ml*	*N/20 FES used by $K_2S_2O_8$ ml*	*$K_2S_2O_8$ taken g*
0.0270	25.00	20.994	4.006	0.0270
0.0470	25.00	18.048	6.952	0.0470
0.0747	25.00	13.954	11.046	0.0747
0.0942	25.00	11.067	13.933	0.0941
0.1186	25.00	7.456	17.544	0.1185

TABLE VI

POTASSIUM CHLORATE

$KClO_3$ taken g	*N/20 FES added ml*	*N/20 $KMnO_4$ used for excess FES ml*	*N/20 FES used by $KClO_3$ ml*	*$KClO_3$ found g*
0.0055	25.00	19.634	5.366	0.0055
0.0072	25.00	17.815	7.185	0.0073
0.0114	25.00	13.818	11.182	0.0114
0.0143	25.00	10.957	14.043	0.0143
0.0195	25.00	5.885	19.115	0.0195

TABLE VII

POTASSIUM BROMATE

$KBrO_3$ taken g	*N/20 FES added ml*	*N/20 $KMnO_4$ used for excess FES ml*	*N/20 FES used by $KBrO_3$ ml*	*$KBrO_3$ found g*
0.0084	20.00	14.008	5.992	0.0083
0.0140	20.00	9.934	10.066	0.0140
0.0170	20.00	7.709	12.291	0.0171
0.0204	33.00	18.343	14.657	0.0204
0.0254	42.00	23.539	18.461	0.0256

TABLE VIII

CERIC SULPHATE

$Ce(SO_4)_2$ taken g	*N/20 FES added ml*	*N/20 $KMnO_4$ used for excess FES ml*	*N/20 FES used by $Ce(SO_4)_2$ ml*	*$Ce(SO_4)_2$ found g*
0.0869	20.00	14.758	5.242	0.0870
0.1705	20.00	9.738	10.262	0.1705
0.2388	20.00	5.630	14.370	0.2388
0.3078	30.00	11.471	18.529	0.3079
0.3325	40.00	19.982	20.018	0.3325

The senior author wishes to acknowledge the help rendered by the junior author, Mr. HARBANS SINGH, B. Sc.; Grad. I.E.E. (London); A.M.Inst. E. (London), especially in setting up the apparatus and increasing the accuracy of potentiometric observations.

SUMMARY

Ferrous ethylenediamine sulphate has been used as a reducing agent to determine indirectly potassium dichromate, hydrogen peroxide, potassium permanganate, potassium persulphate, potassium chlorate, potassium bromate, and ceric sulphate by a potentiometric method. An excess of ferrous ethylenediamine sulphate added to each of the substances in an acid medium is titrated with a standard solution of potassium permanganate, using platinum foil as an oxidation-reduction electrode coupled with a saturated calomel electrode through an agar-agar potassium chloride bridge.

RÉSUMÉ

Le sulfate de fer(II) éthylènediamine a été utilisé comme réducteur pour le dosage potentiométrique indirect du dichromate de potassium, du peroxyde d'hydrogène, des permanganate, persulfate, chlorate et bromate de potassium et du sulfate de cérium(IV). Un excès de sulfate de fer(II)-éthylènediamine est ajouté à chacune de ces substances à doser, en solution acide. Cet excès est ensuite titré au moyen d'une solution étalon de permanganate de potassium, en utilisant une feuille de platine comme électrode d'oxydo-réduction, reliée à une électrode au calomel saturée au moyen d'un pont d'agar-agar-chlorure de potassium.

ZUSAMMENFASSUNG

Das Eisen(II)äthylendiaminsulfat wurde als reduzierende Substanz verwendet für die indirekte potentiometrische Bestimmung von Kaliumbichromat, Wasserstoffsuperoxyd, Kaliumpermanganat Kaliumpersulfat, Kaliumchlorat, Kaliumbromat und Cerium (IV) Sulfat. Ein Überschuss von Eisen (II)äthylendiaminsulfat wird zu jeder der zu bestimmenden Substanzen in einer sauren Lösung gegeben. Dieser Überschuss wird darauf mit Hilfe einer Kaliumpermanganat — Vergleichslösung titriert, indem man eine Oxydo-reduktions-Platinelektrode, eine gesättigte Kalomelelektrode und eine Agar-Agar Brücke mit Kaliumchlorid verwendet.

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ÉTUDE ET DOSAGE POLAROGRAPHIQUE DE LA DI-DNP-HISTIDINE DOSAGE DE L'HISTIDINE

par

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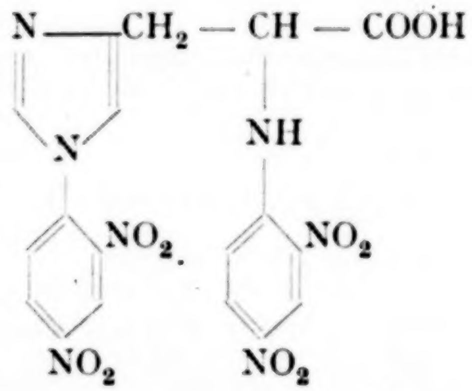
I. PRÉPARATION DE LA DI-DNP-HISTIDINE

Selon SANGER[1], l'histidine réagit quantitativement avec un excès de DNFB pour former la di-DNP-histidine.



C'est en se basant sur ce fait et sur les méthodes de préparation des dérivés DNP d'autres acides aminés, que nous avons synthétisé la di-DNP-histidine.

2 g d'histidine et 4 g de carbonate acide de sodium sont dissous dans un peu d'eau. On ajoute une solution fraîchement préparée de DNFB, en léger excès (7.2 g solubilisés dans un peu d'alcool absolu (99%)). On agite pendant cinq à six heures à température ambiante. On concentre au vide et au bain-marie pour éliminer l'éthanol. Du résidu repris à l'eau, on enlève l'excès de DNFB par extraction à l'éther.

La solution aqueuse est acidifiée avec 70 à 80 ml d'acide chlorhydrique à 3.2%, ce qui précipite la di-DNP-histidine. Le solide jaune, lavé d'abord à l'eau froide, est recristallisé dans l'acétone aqueuse[2]. Nous avons obtenu de cette manière 5 g de produit (rendement 80%, P.F.: 232-4°, ce qui correspond à la valeur donnée dans la littérature.)

Remarque: Nous avons utilisé pour cette synthèse la L-histidine de la maison Hoffmann-La Roche. L'acide chlorhydrique, le carbonate acide de sodium et l'éther étaient des produits „Merck", „pro anal.".

Le % en azote de notre substance, déterminé au micro Dumas, correspond à celui de la di-DNP-histidine.

II. POLAROGRAPHIE DE LA DI-DNP-HISTIDINE

1. Généralités

La di-DNP-histidine est soluble aux pH alcalins. Il n'est donc pas nécessaire d'ajouter de l'alcool éthylique.

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La di-DNP-histidine est solubilisée dans un mélange à volume égal de solution tampon basique et d'eau bidistillée. Elle donne trois sauts polarographiques. Jusqu'à une concentration de 1.6 mg/10 ml, il n'y a pas de maximum. Pour des concentrations supérieures, on observe des maximums aux deuxième et troisième sauts. Pour les éliminer, on ajoute quatre gouttes d'une solution aqueuse à 0.2 % d'alcool polyvinylique.

2. *Composition des solutions*

La di-DNP-histidine dans un mélange à volume égal: eau bidistillée - solution tampon.

Le corps précipitant en milieu acide, nous avons effectué une étude qu'en fonction des pH 8, 9.24, 9.75 et 10. Les tampons sont les mêmes que ceux utilisés lors de l'étude du DNFB[3]. Le tampon de pH 9.75 a été préparé à partir de solutions de carbonate acide et de carbonate neutre de sodium 0.1*M*.

3. *Appareillage, Technique opératoire et résultats*

Polarographe „Sargent XXI"
Hauteur de la colonne de mercure: 17 cm
Temps de chute d'une goutte de mercure (*t*): 2.94 sec
Masse de mercure (*m*): 2.72 mg/sec

Quatre prises de 12 mg de di-DNP-histidine sont introduites dans quatre ballons jaugés de 100 ml. On complète à 100 ml avec un mélange à volume égal: eau bidistillée — tampon. On polarographie.

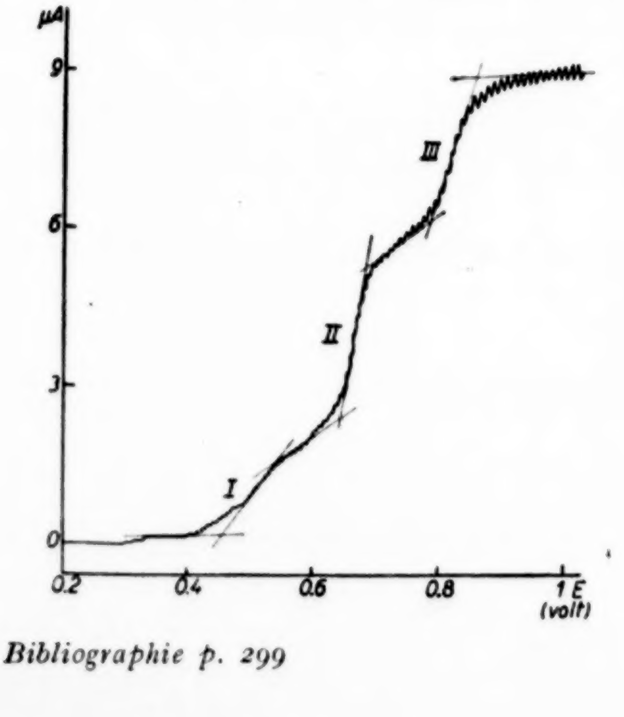
Les résultats obtenus sont donnés dans le Tableau I.

TABLEAU I

12 mg/100 ml di-DNP-histidine

pH	i_1 µA	i_2 µA	i_3 µA	itot µA	$E^1{}_{1/2}$ volt	$E^2{}_{1/2}$ volt	$E^3{}_{1/2}$ volt	i_1/k	i_2/k	i_3/k	itot/k
8	1.9	4.1	4.2	10.2	0.54	0.72	0.88	3.28	7.10	7.25	17.6
9.24	2.1	4.1	4.1	10.3	0.54	0.71	0.86	3.62	7.10	7.10	17.8
9.75	1.9	4.1	4.1	10.1	0.52	0.69	0.83	3.28	7.10	7.10	17.5
10	2.1	4.1	4.1	10.3	0.54	0.70	0.84	3.62	7.10	7.10	17.9

La di-DNP-histidine, à la concentration de 12 mg/100 ml, ne laisse apparaître aucun maximum polarographique. Aux 4 pH choisis, on observe toujours trois sauts (Fig. 1). Les courants de diffusion du deuxième et du troisième sauts sont identiques. Celui du premier est à peu près égal à la moitié du deuxième.



La réduction polarographique de la di-DNP-histidine entre les pH 8 et 10 est donc toujours la même et nécessite le même nombre d'électrons.

La mesure des sauts par la méthode des tangentes est aisée à tous les pH.

Au pH 10, la solution de di-DNP-histidine est stable pendant au moins 48 heures.

4. *Etude logarithmique*

Cette étude, effectuée sur les 3 vagues polarographiques montre que les réactions

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de réduction sont irréversibles. L'obtention de droites dans chaque cas permet de supposer que chaque vague correspond à une seule réduction.

5. *Détermination des électrons échangés*

L'histidine seule, tamponnée à pH 10 ne produit aucun saut. On peut donc supposer que les sauts de la di-DNP-histidine sont dus uniquement à la réduction des fonctions nitro.

A pH 10, la réduction sur la goutte de mercure devrait engager 16 électrons (4 pour chaque fonction nitro) pour fournir 4 fonctions hydroxylamine. Mais on peut aussi supposer que tous les groupes nitro ne se réduisent pas. Un empêchement stérique, par exemple, pourrait éventuellement contrecarrer la réduction d'une ou de deux fonctions nitro. Afin d'éclaircir ce problème, nous avons effectué une étude pour déterminer le nombre d'électrons (n) intervenant dans la réduction polarographique de cette molécule.

Les valeurs de n calculées au moyen de la formule de Heyrovsky-Ilkovic ne peuvent entrer en considération, la réaction n'étant pas réversible. D'autre part nous ne pouvons pas calculer n par la formule d'Ilkovic, car on ne peut évaluer la constante de diffusion (D) pour une molécule aussi compliquée. Nous avons donc utilisé la méthode de REYNOLDS ET SHALGOSKY[5].

Deux prises de di-DNP-histidine, l'une de 48.62 mg et l'autre de 97.24 mg sont introduites dans deux ballons jaugés de 100 ml. On complète au volume avec un mélange à volume égal: eau bidistillée-tampon de pH 10. Ces solutions sont diluées dix fois. Nous obtenons ainsi deux solutions de concentration 10^{-4} et $2 \cdot 10^{-4} M$ (486.2 est le poids moléculaire de l'anion di-DNP-histidine). On polarographie. Les résultats sont portés dans le Tableau II.

TABLEAU II

Conc. de di-DNP-histidine (γ/ml)	*pH*	*E cont. employé (volt)*	*Temps de l'électrolyse (sec.)*	*Volume de la solution (ml)*	*Saut*	i_o *(µA)*	i_t *(µA)*	*n*
48.62	10	1	1200	0.3	III	0.81	0.735	3.4
48.62	10	1	1200	0.3	III	0.81	0.750	4.3
48.62	10	1	2400	0.3	III	0.81	0.720	5.8
2 × 48.62	10	1	1200	0.3	III	1.60	1.440	3.15
2 × 48.62	10	1	1200	0.3	III	1.60	1.420	2.8
2 × 48.62	10	1	2400	0.3	III	1.60	1.340	3.7
2 × 48.62	10	1	2400	0.3	III	1.60	1.360	4.0
48.62	10	1	1200	0.3	II	0.81	0.735	3.4
48.62	10	1	1200	0.3	II	0.81	0.750	4.3
48.62	10	1	2400	0.3	II	0.81	0.705	4.8
2 × 48.62	10	1	1200	0.3	II	1.60	1.440	3.15
2 × 48.62	10	1	1200	0.3	II	1.60	1.420	2.8
2 × 48.62	10	1	2400	0.3	II	1.60	1.320	3.4
2 × 48.62	10	1	2400	0.3	II	1.60	1.360	4.0

Conclusions

Les valeurs du Tableau II correspondent aux deuxième et troisième sauts. Pour le premier nous n'avons malheureusement pas pu obtenir de résultats, les différences entre i_o et i_t étant très petites, des erreurs minimes dans la mesure des sauts entraînent de très grandes variations de n.

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D'ailleurs, pour les deuxième et troisième sauts, on constate déjà de grandes variations dans la valeur de *n* pour de petites différences de courant. Néanmoins, nous pouvons conclure que la réduction polarographique fait intervenir 3 à 4 électrons pour chacun de ces deux sauts. Quant au premier, qui est égal à la moitié du deuxième (et donc du troisième), il faut admettre qu'il nécessite l'apport de 1.5 à 2 électrons.

Malgré le manque apparent de précision il est possible de savoir si ce sont 16 électrons (réduction de 4 fonctions nitro), 12 électrons (réduction de 3 fonctions nitro) ou 8 électrons (réduction de 2 fonctions nitro) qui participent à la réduction de la di-DNP-histidine. Et l'on peut admettre, au vu de nos résultats, que seules deux fonctions nitro sont réduites (8 électrons), ce qui est explicable en admettant un empêchement stérique bloquant la réduction de deux fonctions nitro en ortho.

III. DOSAGE POLAROGRAPHIQUE DE LA DI-DNP-HISTIDINE

Les polarogrammes des solutions contenant plus de 1.6 mg/10 ml de di-DNP-histidine présentent des maximums. C'est la raison pour laquelle nous avons établi deux courbes d'étalonnages, l'une pour des concentrations inférieures à 1.6 mg/10 ml, l'autre pour des concentrations supérieures. Pour ce faire, on pèse 10 mg de di-DNP-histidine dans un ballon jaugé de 100 ml, on complète à 100 ml avec un mélange à volume égal: eau distillée-tampon pH 10. Par dilutions successives de cette solution à l'aide d'une microburette (et au moyen du mélange eau distillée-tampon) on obtient des solutions de concentrations différentes en di-DNP-histidine.

Pour les concentrations supérieures à 1.6 mg/10 ml, nous ajoutons quatre gouttes d'une solution aqueuse d'alcool polyvinylique à 0.2%, pour supprimer les maximums. On élimine l'oxygène par un courant d'hydrogène. Appareillage: voir p. 294.

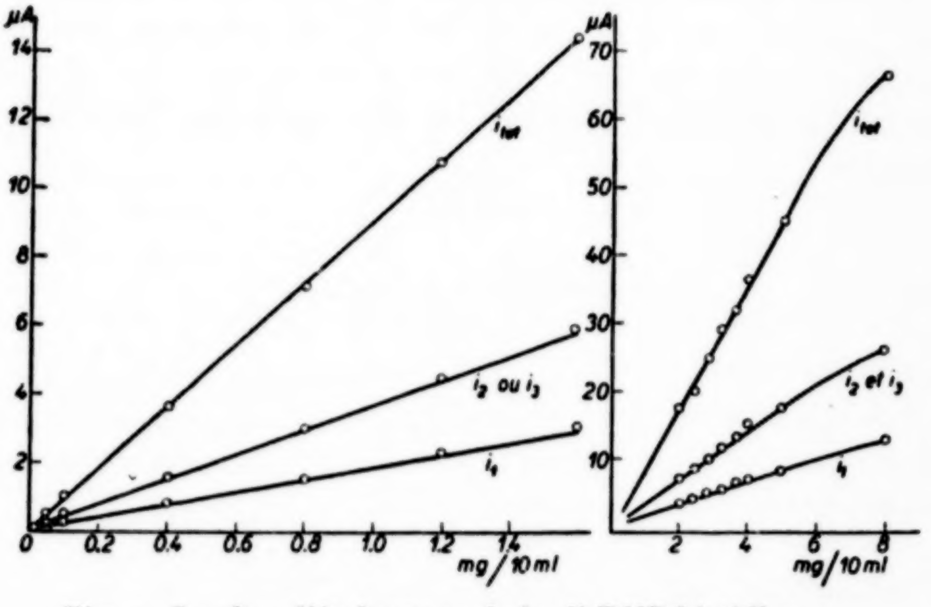

Fig. 2. Courbes d'étalonnage de la di-DNP-histidine.

Les $E_{\frac{1}{2}}$ ont les valeurs moyennes suivantes (par rapport à la surface de mercure)

$$E^1_{\frac{1}{2}} = 0.54,\ E^2_{\frac{1}{2}} = 0.72,\ E^3_{\frac{1}{2}} = 0.84,\ \text{à pH } 10$$

On peut donc doser 0.1 γ dans 0.1 ml de solution, ce qui est réalisable dans une microcuve.

Remarque: Au voisinage de 10 γ le troisième saut n'est plus mesurable.

Pour les concentrations supérieures à 1.6 mg/10 ml et en présence d'alcool polyvinylique, le dosage est possible jusqu'à 5 mg/10 ml ($1.05 \cdot 10^{-3} M$). A partir de cette concentration le courant de diffusion n'est plus une fonction linéaire de la concentration.

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IV DOSAGE DE L'HISTIDINE

Méthode de dosage

Dans un article précédent, nous avons etabli des méthodes de dosage polarographique du DNFB et dans la première partie de celui-ci, le dosage de la di-DNP-histidine. Le DNFB, en milieu bicarbonate de sodium, réagit avec l'histidine pour former la di-DNP-histidine. Pour que la réaction soit quantitative, il faut ajouter un excès de DNFB. Ce dernier est éliminé, après réaction, par extraction à l'éther. La solution contenant la di-DNP-histidine est alors tamponnée au pH 10 avant d'être polarographiée. On peut aussi polarographier l'excès de DNFB extrait à l'éther. Pour ce faire, on évapore ce dernier. Le résidu repris par une solution, à volume égal, tampon pH 10-eau bidistillée, est polarographiée. En déduisant la quantité de DNFB en excès de celle ajoutée à l'histidine, nous pouvons calculer la teneur en histidine.

La courbe d'étalonnage établie pour le dosage de la di-DNP-histidine n'est valable que pour des solutions tamponnées à pH 10. C'est la raison pour laquelle nous avons essayé de faire réagir le DNFB avec l'histidine en solution tampon de pH 10. Ces essais furent négatifs et il faut admettre que le DNFB et l'histidine ne réagissent pas, dans ces conditions, par suite de l'hydrolyse du DNFB. Nous avons travaillé, donc, à un pH inférieur, (solution de carbonate acide de sodium).

TECHNIQUE OPÉRATOIRE ET RÉSULTATS

Solutions utilisées

(1) 24 mg d'histidine dans 10 ml d'eau bidistillée;
(2) 40 mg de carbonate acide de sodium dans 10 ml d'eau bidistillée;
(3) 250 mg de DNFB dans 10 ml d'alcool éthylique à 99%.

On prélève successivement de la solution (1), à l'aide d'une microburette d'un ml:

0.375 ml	soit	0.9	mg d'histidine
0.750 ,,	,,	1.8	,, ,,
1.000 ,,	,,	2.4	,, ,,

que l'on introduit dans trois erlenmeyers de 25 ml. On ajoute à chaque prise 2 ml de la solution (2), soit 8 mg de carbonate acide de sodium et 0.300 ml de la solution (3) (soit 7.5 mg de DNFB). On porte les erlenmeyers dans une étuve à 60° C pendant deux heures.

La réaction étant terminée, on procède à l'extraction à l'éther. Nous utilisons des entonnoirs à robinet de 25 ml. L'extraction se fait avec des portions de 5 ml de solvant.

L'éther ,,pro anal." de la maison ,,Merck" et l'éther ordinaire distillé au laboratoire, ont donné les mêmes résultats.

1. *Solutions pour le dosage de la di-DNP-histidine*

La solution aqueuse contenant la di-DNP-histidine est portée à 40° C dans l'étuve, pour chasser complètement l'éther. On complète le volume à 25 ml avec un mélange, à volume égal, tampon de pH 10-eau bidistillée.

2. *Solutions pour le dosage du DNFB en excès*

La solution éthérée est évaporée dans l'étuve (40° C). Le DNFB résiduel est dissous dans 25 ml d'un mélange, à volume égal, tampon de pH 10-eau bidistillée.

Avant de polarographier ces solutions, on en chasse l'oxygène. Les polarogrammes obtenus permettent de déterminer la quantité de di-DNP-histidine et celle de DNFB en excès, les courbes d'étalonnage étant données précédemment. La teneur en histidine est calculée à partir de l'un ou l'autre de ces résultats.

Essais préliminaires

Pour connaître la quantité de DNFB nécessaire au dosage d'une quantité inconnue d'histidine, il faut procéder à un essai préliminaire.

Pour des quantités d'histidine supérieures à 100 γ, on travaille sur des solutions de 1 ml. On ajoute à ces solutions 200 γ de carbonate acide de sodium et 400 γ de DNFB. On laisse réagir à 60° C pendant deux heures. On ajoute alors progressivement du carbonate acide de sodium et du DNFB (dans le rapport 1:2) jusqu'à apparition d'un trouble dû à l'excès de DNFB non soluble. Ce trouble apparaît en général lorsque la quantité de DNFB est six à huit fois plus grande que celle de l'histidine. Pour de grandes quantités d'histidine (nécessitant plus de 20 mg de DNFB) on fera l'analyse sur une solution d'histidine plus diluée. Pour les quantités d'histidine comprises entre 10 et 100 γ, on travaille sur des solutions d'histidine de 0.1 ml.

L'essai préliminaire achevé, on procédera à l'analyse définitive en utilisant une quantité de DNFB légèrement inférieure à celle trouvée lors de l'essai préliminaire.

Procédant ainsi sur trois échantillons contenant des quantités inconnues d'histidine, nous sommes parvenus aux résultats du Tableau III.

TABLEAU III

Histidine présente	*DNFB ajouté*	*di-DNP-histidine formée*		*Histidine trouvée par formation de di-DNP-histidine*	*Erreur*	*DNFB en excès (mg)*		*Histidine trouvée par l'excès de DNFB*	*Erreur absolue*
		théorique	*trouvée*			*théorique*	*trouvé*		
mg	mg	mg	mg	mg		mg	mg	mg	
1.50	9.00	4.70	4.94	1.56	+0.06	5.40	5.00	1.66	+0.16
4.00	16.00	12.60	12.70	4.07	+0.07	6.40	5.40	4.43	+0.43
2.00	11.00	6.30	6.75	2.15	+0.15	6.20	6.50	1.87	—0.13
γ	γ	γ	γ	γ		γ	γ	γ	
100.0	500.0	314.0	300.0	95.0	—5.0	260.0	260.0	104.0	+4.0
50.0	200.0	157.0	160.0	51.0	+1.0	80.0	90.0	46.0	—4.0
10.0	60.0	31.4	30.0	9.5	—0.5	36.0	37.0	9.6	—0.4

RÉSUMÉ

La di-DNP-histidine a été préparée, puis étudiée au polarographe.

Une courbe d'étalonnage a été établie grâce à laquelle il est possible de doser 1 γ de di-DNP-histidine dans 1 ml.

Une méthode de dosage de l'histidine a été établie. On fait réagir sur celle-ci du DNFB en excès. On élimine l'excès par deux extractions à l'éther. On peut alors déterminer au polarographe soit l'excès de DNFB, soit la di-DNP-histidine formée. Ce procédé permet de doser jusqu'à 10 γ d'histidine.

L'erreur est comprise entre 0.5 et 10% selon la quantité.

SUMMARY

The di-DNP-histidine has been prepared, and studied polarographically.

A standardization curve has been composed by means of which it is possible to estimate 1 γ of di-DNP-histidine in 1 ml.

A method of estimating the histidine has been established. It is allowed to react with an excess of DNFB. The excess is removed by extracting twice with ether. One can then determine polarographically the excess of DNFB, or the di-DNP-histidine formed. By this method up to 10 γ histidine can be determined.

The error lies between 0.5 and 10% according to quantity.

ZUSAMMENFASSUNG

Das Di-DNP-Histidin wurde hergestellt und darauf auf dem Polarograph studiert.

Es wurde eine Eichkurve aufgestellt, dank welcher es möglich ist 1 γ Di-DNP-Histidin in 1 ml zu bestimmen.

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Es wurde eine Methode, um das Histidin zu bestimmen festgesetzt. Man lässt auf diesen Stoff einen Überschuss von DNFB einwirken. Man eliminiert den Überschuss mit zwei Ätherextraktionen. Man kann dann auf dem Polarograph den Überschuss an DNFB oder das gebildete Di-DNP-Histidin bestimmen. Dieser Vorgang erlaubt bis zu 10 γ Histidin zu bestimmen.

Der Fehler liegt zwischen 0.5 und 10% je nach Quantität.

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REVUE DE LIVRES

Substances Naturelles de Synthèse, par **Léon Velluz**, Volume X, Masson et Cie, Paris, 1954, 200 pages avec 1 planche et des tableaux, broché 2300 frs., cartonné toile 2700 frs.

Sous la signature de A. **Allais**, J. **Mathieu**, A. **Petit**, P. **Poirier**, L. **Velluz**, voici le 10ème volume de la collection qui complète la première série. Le sommaire comprend la préparation de la D-L-arginine, la vitamine A, la L-carnosine, le ß-carotène, l'ergothionéine, la D-glucosamine, la D-L-pénicillamine et le rétinène. La 2ème partie comprend l'étude expérimentale avec tableaux de la synthèse peptidique et les synthèses de chaînes isopréniques. La note pratique est relative cette fois aux intermédiaires en synthèse peptidique. Des tableaux indiquent la nocivité de quelques vapeurs de solvants selon **Croswell**, les températures d'auto-ignition et les limites d'inflammabilité de quelques vapeurs, la solubilité de gaz dans les solvants usuels les constantes stalagmométriques de quelques solvants et solutions concentrées. Les tables et les index sont relatifs non seulement à ce volume mais aux numéros VI à X (Le tome V comportait déjà une table récapitulative des numéros I à V).

La lecture ou plutôt l'étude de ce volume X présente un intérêt considérable à cause de la belle étude sur la vitamine A et les carotènes. Les auteurs ont mentionné quelques caractères analytiques à la suite de la partie synthétique proprement dite.

Il m'est venu ensuite l'idée de feuilleter les neuf précédents volumes dont j'ai déjà rendu compte en soulignant leur originalité, leur valeur spécifique, et leur excellente présentation. On reste séduit par la variété des idées soulevées et par le caractère bien vivant des modes opératoires „qui sentent plus la paillasse de laboratoire que le bureau du cabinet de travail". On effectue ainsi un voyage à travers toute la chimie biologique avec des guides ayant le pied sûr, voyage qui fait revivre les découvertes, dignes du kaléidoscope de la petite Alice, effectuées depuis une trentaine d'années.

C. **Duval** (Paris)

Die komplexometrische Titration, von Prof. Dr. G. **Schwarzenbach**, Verlag Enke, Stuttgart, 1955 100 pages, geb. DM 21.—.

La complexométrie est depuis ces derniers dix ans une nouvelle technique des plus importantes de la chimie analytique. Elle a trouvé de nombreuses applications dans les laboratoires, soit scientifiques, soit industriels. Le livre de **Schwarzenbach** est une publication originale, les complexons et leurs élégantes applications étant dus presque entièrement au professeur zurichois.

La partie théorique traite: les complexons, les possibilités titrimétriques, les courbes de titration, les indicateurs et de généralités sur la titration simultanée de plusieurs ions. Tous ces chapitres sont développés d'une manière impeccable en se basant sur la chimie-physique; cependant, on a parfois l'impression que le style de l'auteur est quelque peu compliqué.

La partie pratique contient les applications de la complexométrie. On y trouve trente modes opératoires environ. Les remarques de l'auteur concernant les ions gênants lors de titrations particulières sont fort utiles. La littérature est complète jusqu'à l'automne 1954; 181 publications sont signalées. Il faut citer encore la liste de symboles physico-chimiques utilisés dans ce livre, judicieusement placée après la préface. Le papier et l'impression sont excellents. En résumé, c'est un livre important et indispensable à chaque analyste moderne.

C. **Jegge** (Genève)

VOLUMETRIC STUDIES IN OXIDATION-REDUCTION REACTIONS
IV. OXIDATION WITH CHLORAMINE-T. IODINE MONOCHLORIDE METHOD

by

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NOLL[1] described the use of chloramine-T as an oxidizing reagent. RUPP[2] used chloramine-T for the determination of trivalent antimony, and later for the determination of stannous tin. TOMICEK AND SUCHARDA[3] used it as a reagent for the potentiometric determination of trivalent arsenic and antimony; bivalent tin and iron and ferrocyanide and iodide ions; and for the visual titration of trivalent arsenic and antimony, using methyl red as an indicator. KOMAROWSKY *et al.*[4] have shown that chloramine-T can be used as a volumetric reagent to replace the more expensive iodine and less stable hypochlorite in the estimation of ferrocyanide, hydrazine and hypophosphite. SINGH AND REHMANN[5] have used chloramine-T for the determination of hydroquinone, quinhydrone, hydrazine hydrochloride, potassium iodide, sodium bisulphite and sodium nitrite by a potentiometric method. LEE[6] *et al.* used chloramine-T in the quantitative estimation of various organic sulphides. AFANAS'EV[7] has shown that chloramine-T is a suitable reagent for determining many organic compounds by oxidative volumetric procedure, using methyl red or indigocarmine as an indicator. SINGH *et al.*[8] have used chloramine-T for the potentiometric estimations of vanilin, *p*-hydroxybenzaldehyde, benzaldehyde, salicylaldehyde, acetaldehyde, furfural, urea, oxalic acid, thiourea, glycerol and mannitol.

In the present investigation chloramine-T has been used for the volumetric determination of potassium iodide, hydrazine sulphate, arsenious oxide, stannous chloride, mercurous chloride, tartar emetic, potassium thiocyanate, and ferrous ammonium sulphate.

In presence of hydrochloric acid these substances react with chloramine-T in accordance with the equations:

$$\begin{aligned}
&\mathrm{KI + CH_3C_6H_4SO_2N(Na)Cl + 2\,HCl} &&= \mathrm{KCl + NaCl + ICl + CH_3C_6H_4SO_2NH_2}\\
&\mathrm{N_2H_4 + 2\,CH_3C_6H_4SO_2N(Na)Cl} &&= \mathrm{N_2 + 2\,NaCl + 2\,CH_3C_6H_4SO_2NH_2}\\
&\mathrm{As_2O_3 + 2\,CH_3C_6H_4SO_2N(Na)Cl + 2H_2O} &&= \mathrm{As_2O_5 + 2\,NaCl + 2\,CH_3C_6H_4SO_2NH_2}\\
&\mathrm{SnCl_2 + CH_3C_6H_4SO_2N(Na)Cl + 2HCl} &&= \mathrm{SnCl_4 + NaCl + CH_3C_6H_4SO_2NH_2}\\
&\mathrm{Hg_2Cl_2 + CH_3C_6H_4SO_2N(Na)Cl + 2HCl} &&= \mathrm{2\,HgCl_2 + NaCl + CH_3C_6H_4SO_2NH_2}\\
&\mathrm{Sb_2O_3 + 2\,CH_3C_6H_4SO_2N(Na)Cl + 2H_2O} &&= \mathrm{Sb_2O_5 + 2\,NaCl + 2\,CH_3C_6H_4SO_2NH_2}\\
&\mathrm{2KCNS + 6CH_3C_6H_4SO_2N(Na)Cl + 8H_2O} &&= \mathrm{2KHSO_4 + 2HCN + 6NaCl +}\\
& &&\qquad\mathrm{6CH_3C_6H_4SO_2NH_2}\\
&\mathrm{6FeSO_4 + 3CH_3C_6H_4SO_2N(Na)Cl + 6HCl} &&= \mathrm{2Fe_2(SO_4)_3 + 2FeCl_3 + 3NaCl +}\\
& &&\qquad\mathrm{3CH_3C_6H_4SO_2NH_2}
\end{aligned}$$

References p. 304.

EXPERIMENTAL

A known weight of each substance was taken in a conical flask and about 25 ml of water, 25 ml of concentrated hydrochloric acid, 5 ml of 0.02*M* iodine monochloride and 5 ml of chloroform were added to it. The mixture was titrated against standard chloramine-T solution. The reagent was added from a burette until the solution, which was coloured with iodine, became pale yellow and the chloroform layer acquired a purple colour. The conical flask was stoppered and vigorously shaken during the titration. Addition of small volumes of the chloramine-T solution was continued, shaking vigorously after each addition, until the chloroform layer was faintly violet. The chloramine-T was then added dropwise, with shaking after the addition of each drop, till the chloroform layer became very pale yellow. The end-point was very sharp.

In these titrations normality of the solution with respect to hydrochloric acid was kept between 4*N* to 6*N*. Several titrations were performed in each case. From the volume of chloramine-T used, corresponding to the end-point in each titration, the amount of the substance was calculated. The results are recorded in the following tables.

All the chemicals used in this investigation were of guaranteed purity.

TABLE I

POTASSIUM IODIDE

KI taken g	*0.1000N chloramine-T used* ml	*KI found* g
0.0831	10.00	0.0830
0.1496	18.00	0.1494
0.1828	22.00	0.1826
0.2244	27.00	0.2241
0.2660	32.05	0.2661

TABLE II

HYDRAZINE SULPHATE

$N_2H_4.H_2SO_4$ *taken* g	*0.1000N chloramine-T used* ml	$N_2N_4.H_2SO_4$ *found* g
0.0490	15.10	0.0491
0.0720	22.10	0.0719
0.0878	27.00	0.0878
0.1043	32.10	0.1044
0.1206	37.00	0.1204

TABLE III

ARSENIOUS OXIDE

As_2O_3 *taken* g	*0.1000N chloramine-T used* ml	As_2O_3 *found* g
0.0496	10.00	0.0495
0.0893	18.10	0.0895
0.1088	22.00	0.1088
0.1339	27.10	0.1340
0.1588	32.10	0.1588

TABLE IV

STANNOUS CHLORIDE

$SnCl_2.2\,H_2O$ *taken* g	*0.1000N chloramine-T used* ml	$SnCl_2.2\,H_2O$ *found* g
0.1129	10.00	0.1128
0.2034	18.00	0.2031
0.2486	22.00	0.2482
0.3048	27.00	0.3046
0.4068	36.05	0.4067

References p. 304.

TABLE V

MERCUROUS CHLORIDE

Hg_2Cl_2 *taken* g	0.1000N *chloramine-T used* ml	Hg_2Cl_2 *found* g
0.2361	10.00	0.2361
0.3542	15.00	0.3541
0.5194	22.00	0.5194
0.6375	27.00	0.6374
0.7555	32.00	0.7554

TABLE VI

TARTAR-EMETIC

Tartar-emetic taken g	0.1000N *chloramine-T used* ml	*Tartar-emetic found* g
0.1670	10.00	0.1670
0.3006	18.00	0.3005
0.4175	25.00	0.4174
0.5343	32.00	0.5343
0.6680	40.00	0.6679

TABLE VII

POTASSIUM THIOCYANATE

KCNS taken g	0.1000N *chloramine-T used* ml	*KCNS found* g
0.0162	10.00	0.0162
0.0294	18.00	0.0292
0.0406	25.00	0.0405
0.0520	32.00	0.0518
0.0730	45.00	0.0729

TABLE VIII

FERROUS AMMONIUM SULPHATE

$FeSO_4(NH_4)_2SO_4.6H_2O$ *taken* g	0.1000N *chloramine-T used* ml	$FeSO_4(NH_4)_2SO_4.6H_2O$ *found* g
0.2353	6.00	0.2353
0.3922	10.00	0.3922
0.5884	15.00	0.5882
0.7880	20.10	0.7882
0.9452	24.10	0.9451

The results show that the substances given in Tables I to VIII can be determined quantitatively by the iodine monochloride method, using chloramine-T as oxidizing agent.

SUMMARY

Chloramine-T has been used as an oxidizing agent in hydrochloric acid medium for the volumetric estimations of potassium iodide, hydrazine sulphate, arsenious oxide, stannous chloride, mercurous chloride, tartar-emetic, potassium thiocyanate and ferrous ammonium sulphate, using iodine monochloride as a catalyst and pre-oxidizer. Chloroform is used as an indicator. It is coloured pink owing to the liberation of iodine during the titration and becomes very pale yellow at the end-point because of the formation of iodine monochloride.

RÉSUMÉ

La chloramine-T a été utilisée comme oxydant, en solution chlorhydrique, pour le dosage volumétrique de l'iodure de potassium, du sulfate d'hydrazine, de l'anhydride arsénieux, du chlorure

d'étain(II), du chlorure de mercure(I), du tartrate d'antimonyle, du thiocyanate de potassium et du sulfate de fer(II) et d'ammonium; on emploie le monochlorure d'iode comme catalyseur et préoxydant. Le chloroforme sert d'indicateur; il se colore en violet par l'iode libéré pendant la titration et devient jaune pâle au point final par formation de monochlorure d'iode.

ZUSAMMENFASSUNG

Das Chloramin-T wurde in salzsaurer Lösung als Oxydationsmittel verwendet für die volumetrische Bestimmung von Kaliumiodid, Hydrazinsulfat, arseniger Säure, Zinn (II) chlorid, Quecksilber (I) chlorid, Antimonyltartrat, Kaliumthiocyanat und Eisen (II) — und Ammoniumsulfat. Man verwendet das Jodmonochlorid als Katalisator und voroxydierendes Mittel. Das Chloroform dient als Indikator; es färbt sich violet durch das während der Titration frei gewordene Jod und wird am Endpunkt durch Bildung von Jodmonochlorid hellgelb.

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VOLUMETRIC STUDIES IN OXIDATION-REDUCTION REACTIONS
V. OXIDATION WITH CHLORAMINE-T. INDIRECT DETERMINATIONS

by

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In the present investigation an attempt has been made to determine indirectly hydrogen peroxide, lead dioxide, selenium dioxide, sodium formate, potassium metaperiodate, potassium permanganate and potassium dichromate by a volumetric method, using chloramine-T as an oxidizing agent[1].

In all titrations with chloramine-T, 5 ml of 0.02*M* iodine monochloride, 5 ml of chloroform and sufficient hydrochloric acid to keep its normality between 4*N* and 6*N* were added to the titrant in a conical flask. Chloramine-T was added from a burette until the solution which was first coloured with iodine became pale yellow. The conical flask was then stoppered and vigorously shaken. Addition of small volumes of chloramine-T solution was continued, shaking vigorously after each addition until the chloroform layer became faintly violet. The reagent was then added dropwise, with shaking after the addition of each drop, until the chloroform layer changed its colour from violet to very pale yellow. The end-point was very sharp.

1. *Determination of hydrogen peroxide*

A known amount of hydrogen peroxide was transferred to a conical flask and a known excess of arsenious oxide, dissolved in 10% sodium hydroxide solution, was added to it. The mixture was allowed to stand for a couple of minutes and was acidified with concentrated hydrochloric acid. The excess of arsenious oxide, left unreacted in the mixture, was determined by titrating it against standard chloramine-T solution. The results are given in Table I.

TABLE I

HYDROGEN PEROXIDE

H_2O_2 *taken* g	*N/10* As_2O_3 *added* ml	*N/10 Chloramine-T used for excess* As_2O_3 ml	*N/10* As_2O_3 *used by* H_2O_2 ml	H_2O_2 *found* g
0.0255	20.00	5.05	14.95	0.0254
0.0306	25.00	7.00	18.00	0.0306
0.0374	30.00	8.10	21.90	0.0372
0.0459	35.00	7.90	27.10	0.0461
0.0544	40.00	8.00	32.00	0.0544

2. *Determination of lead dioxide*

A known amount of the dioxide was transferred to a conical flask and a known excess of potassium iodide solution was added to it. The excess of potassium iodide was back-titrated with standard chloramine-T solution. The results are recorded in Table II.

TABLE II

LEAD DIOXIDE

PbO_2 taken g	*$M/20$ KI added* ml	*$N/10$ Chloramine-T used for excess KI* ml	*$M/20$ KI used by PbO_2* ml	*PbO_2 found* g
0.0960	15.00	7.00	8.00	0.0957
0.1440	20.00	8.00	12.00	0.1435
0.1806	25.00	9.90	15.10	0.1806
0.2160	27.00	8.95	18.05	0.2159
0.2584	30.00	8.40	21.60	0.2583

3. *Determination of selenium dioxide*

A known weight of selenium dioxide was dissolved in a minimum quantity of hot water and known excess of $M/10$ hydrazine sulphate solution was added to it. The mixture was heated to boiling. The selenium that separated was removed by filtration. The unused hydrazine sulphate left in the filtrate was titrated against standard chloramine-T. The results are given in Table III.

TABLE III

SELENIUM DIOXIDE

SeO_2 taken g	*$M/10$ $N_2H_4.H_2SO_4$ added* ml	*$N/10$ Chloramine-T used for excess $N_2H_4.H_2SO_4$* ml	*$M/10$ $N_2H_4.H_2SO_4$ used by SeO_2* ml	*SeO_2 found* g
0.0890	10.00	8.00	8.00	0.0888
0.1110	13.00	12.00	10.00	0.1110
0.1560	18.00	16.00	14.00	0.1554
0.1995	21.00	12.00	18.00	0.1998
0.2220	25.00	20.00	20.00	0.2220

4. *Determination of sodium formate*

A known amount of sodium formate was transferred to a conical flask. Some sodium acetate solution, and excess of saturated mercuric chloride solution and sufficient water to bring the volume to about 75 ml were added to it. The mixture was heated on a steam-bath for about two hours until no more carbon dioxide was evolved. The flask was cooled and the precipitated mercurous chloride was filtered. The precipitate along with the filter paper was transferred to a conical flask, and titrated against standard chloramine-T. The results are given in Table IV.

TABLE IV

SODIUM FORMATE

HCOONa taken g	*$N/10$ Chloramine-T used* ml	*HCOONa found* g
0.0272	8.00	0.0272
0.0476	14.05	0.0478
0.0612	17.95	0.0610
0.0750	22.00	0.0748
0.0850	25.00	0.0850

5. *Determination of potassium meta-periodate*

A known weight of potassium meta-periodate was transferred to a conical flask and a known excess of arsenious oxide, dissolved in 10% sodium hydroxide solution, was added to it. The mixture was acidified with concentrated hydrochloric acid. The excess of arsenious oxide left unreacted in the mixture was determined by titrating it against standard chloramine-T solution. The results are given in Table V.

TABLE V

POTASSIUM META-PERIODATE

KIO_4 taken g	N/10 As_2O_3 added ml	N/10 Chloramine-T used for excess As_2O_3 ml	N/10 As_2O_3 used by KIO_4 ml	KIO_4 found g
0.0384	18.00	8.00	10.00	0.0383
0.0538	24.00	10.00	14.00	0.0537
0.0691	28.00	10.00	18.00	0.0690
0.0845	30.00	8.00	22.00	0.0844
0.0960	37.00	11.90	25.10	0.0962

6. *Determination of potassium permanganate*

A known amount of potassium permanganate was dissolved in water and a known excess of ferrous ammonium sulphate solution was added to it. The mixture was acidified with sulphuric acid. The excess of ferrous ammonium sulphate left unreacted was titrated back with standard chloramine-T solution. The results are recorded in Table VI.

TABLE VI

POTASSIUM PERMANGANATE

$KMnO_4$ taken g	N/10 $FeSO_4(NH_4)_2SO_4$. 6 H_2O added ml	N/10 Chloramine-T used for excess $FeSO_4$ $(NH_4)_2SO_4$. $6H_2O$ ml	N/10 $FeSO_4(NH_4)_2SO_4$. 6 H_2O used by $KMnO_4$ ml	$KMnO_4$ found g
0.0318	18.00	8.00	10.00	0.0316
0.0474	20.00	5.00	15.00	0.0474
0.0633	28.00	8.00	20.00	0.0632
0.0884	35.00	7.00	28.00	0.0885
0.1108	45.00	10.00	35.00	0.1106

7. *Determination of potassium dichromate*

A known amount of potassium dichromate was dissolved in water and a known excess of ferrous ammonium sulphate was added to it. The mixture was acidified with sulphuric acid. The excess of ferrous ammonium sulphate, left unreacted in the mixture, was titrated against standard chloramine-T solution. The results are given in Table VII.

TABLE VII

POTASSIUM DICHROMATE

$K_2Cr_2O_7$ taken g	N/10 $FeSO_4(NH_4)_2SO_4$. 6 H_2O added ml	N/10 Chloramine-T used for excess $FeSO_4(NH_4)_2SO_4.6H_2O$ ml	N/10 $FeSO_4(NH_4)_2SO_4$. $6H_2O$ used by $K_2Cr_2O_7$ ml	$K_2Cr_2O_7$ found g
0.0490	18.00	8.00	10.00	0.0490
0.0688	20.00	6.00	14.00	0.0687
0.0884	25.00	7.00	18.00	0.0883
0.1080	30.00	8.00	22.00	0.1079
0.1322	35.00	8.00	27.00	0.1324

From the results given in Tables I to VII, it is evident that chloramine-T can be used as a volumetric reagent to determine indirectly hydrogen peroxide, lead dioxide, selenium dioxide, sodium formate, potassium meta-periodate, potassium permanganate and potassium dichromate.

SUMMARY

Chloramine-T has been used as an oxidizing agent in hydrochloric acid medium for the indirect volumetric determination of hydrogen peroxide, lead dioxide, selenium dioxide, sodium formate, potassium meta-periodate, potassium permanganate and potassium dichromate using iodine monochloride as a catalyst, preoxidizer and an indicator. Chloroform is coloured pink owing to the liberation of iodine during the titration and becomes very pale yellow at the end-point because of the formation of iodine monochloride.

RÉSUMÉ

La chloramine-T a été utilisée comme oxydant, en milieu chlorhydrique, pour le dosage volumétrique indirect du peroxyde d'hydrogène, du dioxyde de plomb, du dioxyde de sélénium, du formiate de sodium, des métaperiodate, permanganate et dichromate de potassium. On emploie le monochlorure d'iode comme catalyseur et pré-oxydant. Le chloroforme, choisi comme indicateur, se colore en violet par l'iode libéré pendant la titration et devient jaune pâle au point d'équivalence, par formation de monochlorure d'iode.

ZUSAMMENFASSUNG

Das Chloramin-T wurde in salzsaurem Milieu als Oxydationsmittel verwendet für die indirekte volumetrische Bestimmung von Wasserstoffperoxyd, Bleidioxyd, Selendioxyd, Natriumformiat, Metaperiodat, Kaliumpermanganat und Kaliumbichromat. Man verwendet das Jodmonochlorid als Katalysator und voroxydierendes Mittel. Das Chloroform, welches als Indikator gewählt wurde, färbt sich durch das während der Titration frei gewordene Jod violett und wird am Umschlagspunkt durch die Bildung von Jodmonochlorid hellgelb.

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TITRIMETRIC DETERMINATION OF ALUMINIUM IN STEEL

by

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INTRODUCTION

In a recent paper[1] we described a gravimetric procedure for the determination of aluminium in plain steels. This method involved the separation of iron from the sample using dichlorodiethylether and was so successful in this respect that it was decided to extend the method by using a titrimetric or colorimetric finish.

The titrimetric finish which was examined was that based on the complexing of aluminium ion fluoride[2,3].

The method was based on an acid-base titration of Al^{+3} first in the absence of fluoride and then in the presence of fluoride.

Early methods were based on the equations:-

$$AlCl_3 + 3\ NaOH \rightarrow Al(OH)_3 + 3\ NaCl \quad \text{(1)}$$

$$Al(OH)_3 + 6\ NaF \rightarrow Na_3[AlF_6] + 3\ NaOH \quad \text{(2)}$$

but different workers were unable to agree on the choice of indicator and the conditions of titration. Low results were frequently obtained and these were considered to be caused by the formation of basis salts such as $Al(OH)_2Cl$.

In a more recent paper[4] BECK AND SZABO overcame this difficulty in the following manner.

The solution was made slightly caustic and equal aliquots were then taken. The first aliquot was titrated with hydrochloric acid. To the second aliquot excess sodium fluoride was added and the solution titrated to the same end-point as before. The equations on which this was based are as follows:-

$$Na_3AlO_3 + 3\ HCl \rightarrow Al(OH)_3 + 3\ NaCl \quad \text{(3)}$$

$$Na_3AlO_3 + 6\ NaF + 3\ H_2O \rightarrow Na_3[AlF_6] + 6\ NaOH \quad \text{(4)}$$

The addition of fluoride means that three extra molecules of hydrochloric acid are required in the titration for each molecule of aluminium present.

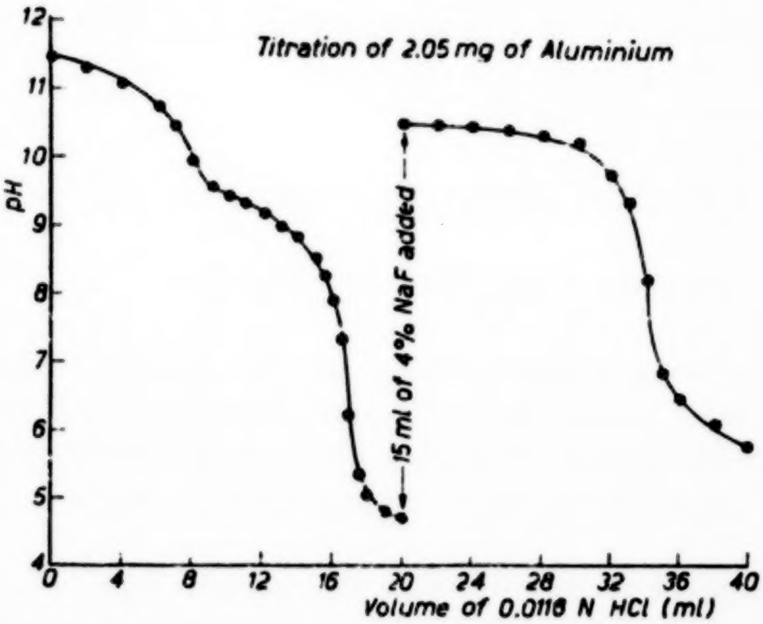
They recommended that a five times excess of fluoride should be used and that neutral red should be used as indicator. This paper appeared to show promise and work was carried out to apply the method to steel analysis.

Investigation carried out

There were several points in BECK AND SZABO's paper which were not clear. For example in Table II of their paper[4] calculation of the amounts of aluminium found from their titration results do not agree with the figures they have published and in fact deviate significantly from the theoretical figure quoted. They also recommend taking aliquots of the original solution. This is time-consuming and can introduce errors when used as a routine method; steps were therefore taken to overcome this. The interferences they noted from carbonate and silica were confirmed and their recommendation to use a five times excess of fluoride was adhered to.

Analysis on single solutions

Titrations were carried out on a single solutions as follows. The solution was made slightly alkaline with a caustic soda. Standard hydrochloric acid was then run in until the solution had passed the end-point. The change in pH was plotted using a pH meter. Sodium fluoride was then added in excess and the solution boiled to ensure that the reaction was complete. It was then cooled to displace the equilibrium in favour of the complex formation. The solution was then titrated again with the standard hydrochloric acid, and as before the pH was plotted. The pH curve obtained is shown in Fig. 1.



It can be seen that the two curves are not quite parallel but if the acid is standardized with a given indicator against a standard aluminium solution, reproducible results should be obtained. For this reason cresol red and thymol blue were used as indicator.

Reproducible results were obtained on mixture of pure iron and aluminium salts. On applying the method to steel analysis however, the other elements present caused poor results to be obtained. Their presence was eliminated by precipitating the remaining iron and aluminium with ammonia/ammonium chloride mixture, filtering and proceeding with the dissolved precipitate. It was found necessary to wash away ammonium salts from the precipitate with sodium chloride solution, otherwise ammonia was driven off when boiling before the last titration and the pH of the solution was disturbed causing poor results to be obtained.

Briefly the method evolved was as follows: —

After extraction of the bulk of the iron, the remaining iron and aluminium were precipitated and filtered. The precipitate was washed free from ammonia with sodium chloride solution and then dissolved in dil. hydrochloric acid. Excess sodium hydroxide was then added and the solution titrated to the first end-point using cresol red/thymol blue as indicator. Sodium fluoride was added to the solution which was then boiled, cooled and titrated again with hydrochloric acid to the same end-point as before. From the volume of standard hydrochloric acid required after fluoride addition the quantity of aluminium present in the solution can be calculated.

Results

The results obtained are listed in Table I.

TABLE I

Al in steel mg	*Al added* mg	*Total Al* mg	*Al found* mg
0.04	nil	0.04	0.04
0.04	nil	0.04	0.04
0.04	nil	0.04	0.05
0.04	0.41	0.45	0.41
0.04	0.41	0.45	0.41
0.04	0.41	0.45	0.40
0.04	4.49	4.53	4.40
0.04	4.49	4.53	4.40
0.04	4.49	4.53	4.54
0.04	27.00	27.05	26.7
0.04	27.00	27.05	27.1

RECOMMENDED PROCEDURE

Reagents

ββ'. dichlor diethyl ether	Technical reagent purified by steam distillation.
Hydrochloric acid	Concentrated analytical reagent.
Nitric acid	Concentrated analytical reagent.
Ammonium chloride solid	Analytical reagent.
„ „ solution	1% w/v in water.
Sodium chloride solution	1% w/v in water.
Ammonia	50% v/v 0.880 s.g. ammonia in water.
Sodium hydroxide solution	Approx. $N/5$ NaOH carbonate free.
Sodium fluoride solution	4% w/v sodium fluoride in water. The solution should be neutral to the indicator used.
Standard $0.1N$ hydrochloric acid	Reagents standardized against known quantities of aluminium.
Standard $0.01N$ hydrochloric acid	

Indicator.

Mixture of equal parts of 0.2% solution of cresol red and thymol blue in water.

Procedure

Dissolve 5 g of steel in hydrochloric acid and oxidize with nitric acid. Evaporate to a paste, cool and make up to 50 ml with conc. hydrochloric acid, the solution should now be about $9N$ HCl. Transfer to a separating funnel washing out with the minimum of conc. hydrochloric acid and shake with 100 ml of dichlorodiethyl ether. Discard the lower (ether) layer and repeat the extraction with two further samples of dichlorodiethyl ether.

References p. 312.

Transfer the remaining to a 125 ml beaker and evaporate to dryness without baking. Dissolve in hydrochloric acid and dilute to 10-20 ml, filter off any silica, washing with dil. hydrochloric acid. Adjust the volume of the filtrate to 50-100 ml. Add solid ammonium chloride (2-3 g), boil and add sufficient ammonia to precipitate aluminium, *etc.* Boil for a further five minutes, filter through a No. 41 paper and wash with ammonium chloride solution until free from Mn, Ni, *etc.*, then wash with sodium chloride solution until free from ammonium salts. Redissolve the precipitate in hydrochloric acid and boil off any excess.

Dilute to about 20 ml add two drops of indicator and make alkaline with carbonate-free sodium hydroxide ($N/5$). If sufficient iron is present to interfere with the detection of the end-point, dilute still further and add a little paper pulp.

Run in standard hydrochloric acid until the indicator changes to yellow and note the burette reading. Add excess sodium fluoride solution, at least 5 ml per 1 mg of aluminium, boil and cool to the temperature at which the first titration was carried out (room temperature). Titrate with standard acid to the same colour as before and record the difference in the two burette readings.

$$1 \text{ ml } N/10 \text{ HCl} = 0.899 \text{ mg Al}$$

Standardization of acid solution

The procedure outlined above must be followed to standardize the acid against a known aluminium solution. From this point of view it might successfully be argued that the conversion factor for ml of acid to mg of aluminium is empirical since the wrong answer is obtained when the acid is standardized in the normal way. It was also found that the factor varied slightly for different quantities of aluminium and it was found advisable to standardize the acid against known quantities of aluminium similar to that in the sample.

Remarks

When large quantities of fluoride were used, the end-point was difficult to judge, this limited the application of the method to rather small quantities of aluminium. It was also found that the indicator changed colour at a slightly higher pH in the presence of fluoride. Error caused by this is reduced when the acid is standardized in the recommended method.

ACKNOWLEDGEMENTS

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SUMMARY

A titrimetric method has been worked out for the determination of aluminium in plain steels using dichlorodiethyl ether to separate off the iron and titrating with hydrochloric acid first in the absence and then in the presence of fluoride.

RÉSUMÉ

Une méthode titrimétrique a été établie pour le dosage de l'aluminium dans des aciers. On effectue une séparation du fer au moyen de l'éther dichlorodiéthylique et on dose l'aluminium par titration au moyen de l'acide chlorhydrique, d'abord en l'absence, puis en présence de fluor.

ZUSAMMENFASSUNG

Eine titrimetrische Methode wurde ausgearbeitet, um Aluminium in Stahl zu bestimmen. Man nimmt eine Trennung des Eisens vor mit Hilfe von Dichlorodiäthyläther und bestimmt dann das Aluminium durch Titration mit Salzsäure, zuerst in Abwesenheit, nachher in Gegenwart von Fluor.

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OXIDIMETRIC METHODS FOR THE VOLUMETRIC ESTIMATION OF SULPHITE

by

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One of the common reagents employed for the estimation of sulphite or sulphurous acid is iodine. BUNSEN[1] AND VOLHARD[2] appear to be pioneer investigators on this subject. RASCHIG[3] pointed out the risk of aerial oxidation of sulphite during the titration of sulphurous acid by iodine in bicarbonate solution. He stated that correct results are obtained only when sulphurous acid or its salt solutions are allowed to flow into excess of iodine solution and the excess titrated with standard thiosulphate solution. While confirming RASCHIG'S work, KOLTHOFF[4] states that a direct titration of sulphurous acid or its salts with iodine in the burette gives incorrect values, even after protecting the sulphite solutions from oxidation by air with negative catalysts like mannitol or alcohol. According to him, very good results are obtained by letting the solution to be titrated flow from a burette into a measured quantity of iodine until it is decolorised. JAMIESON[5] proposed estimating sulphite by the potassium iodate method of L. W. ANDREWS in strong hydrochloric acid medium. The reaction is as follows:

$$KIO_3 + 2\ SO_2 + 2\ HCl + H_2O \rightarrow 2\ H_2SO_4 + ICl + KCl$$

SCHWICKER[5] proposed running down the sulphite solution into an acidified solution of potassium iodate, until iodine is just formed as shown by the starch indicator added towards the end. The sulphite solution is stabilized by the addition of 5-10% alcohol. The reaction is stated by SCHWICKER to be as follows

$$3\ SO_3^{-2} + IO_3^{-} \rightarrow 3\ SO_4^{-2} + I^{-}$$

HENDRIXSON[6] found that the bromate method gives low values perhaps owing to the formation of dithionate, which resists further oxidation.

PEAN DE ST GILLES[7] investigated the action of permanganate on sulphurous acid in acid solution and stated that sulphuric and dithionic acids are the products.

GELIS[8] found that the proportion of dithionic acid formed in this reaction depends on the acid concentration and temperature. LUNGE AND SMITH[9] ascribed the discrepancy to loss of sulphur dioxide by volatilisation. DYMOND AND HUGHES[10] showed that the discrepancy is only due to the formation of dithionic acid. HONIG AND ZATZEK[11] found that sulphite is not oxidized completely by permanganate to sulphate in acid solution but only in neutral or alkaline solution. According to PINNOW[12] the results vary from 90.9% in acid solution to 97.2% in alkaline solution. HENDRIXSON AND VERBECK[13] carried out the electrometric titration of sulphite with permanganate in a hydrogen atmosphere, running down the sulphite from the burette into the permanganate in a medium kept about 1*N* in sulphuric acid. They obtained results varying from 89.6% to 93% and expressed their opinion that the method is impracticable. HENDRIXSON[6] found almost the same deficiency when sulphite was added to excess of alkaline permanganate.

LANG AND KURTENACKER[14] have investigated the use of ceric sulphate solution for the estimation of sulphite in two different ways. (1) The sulphite solution was directly titrated with decinormal ceric sulphate solution, using starch potassium iodide indicator towards the end. (2) The sulphite solution was added to a measured quantity of excess ceric sulphate solution, kept for ten minutes and the excess ceric sulphate solution backtitrated with decinormal ferrous sulphate solution using ferroin as indicator. In the first method they found that 72-86% of sulphite was converted to dithionate, and the remaining 28-14% to sulphate, according to the experimental conditions; in the second procedure a much larger percentage of sulphite was converted to sulphate. Nevertheless, even the second method has been found to be unsatisfactory as it gives values lower than the theoretical.

LANG AND KURTENACKER (*loc. cit.*) also carried out experiments on the use of ferric chloride and ferric sulphate as oxidizing agents. The sulphite solution was run into an excess of the ferric chloride solution, kept for ten minutes more than the time required for the disappearence of the initial red-brown colour and the ferrous salt formed was titrated with ceric sulphate solution. The results were found to be too low, the error in the majority of the experiments being 5-7%, sometimes reaching 10%. If the iron solution was acidified with 1*N* hydrochloric acid the error rose to about 25%. When the same procedure was adopted with ferric sulphate containing 1*N* H_2SO_4 some loss of sulphur dioxide was noticed. In one experiment, it was found that about 47% sulphite was transformed into sulphate, about 39% into dithionate and about 14% was lost as sulphur dioxide. I. N. KUZNINKH AND T. W. BOMSTEIN[15] studied the catalytic effect of Cu^{+2} on the reaction between ferric sulphate and sulphur dioxide in aqueous solution. After examining the use of potassium dichromate for the estimation of sodium sulphite, HENDRIXSON[6] stated that the errors are about the same as with the permanganate method; and that the cause of the error is due to a partial oxidation of sulphite to dithionate. BONNER AND YOST[16] have summarized the relative merits of a number of methods as follows:-

TABLE I

Oxidant used	*Percentage error*
Permanganate	9.0
Dichromate	2.8
Hypochlorous acid	2.2
Sodium bromate	3.3
Potassium iodate	nil
Bromine	nil

A. R. VASUDEVA MURTY[17] reports that sulphite is oxidized to sulphate quantitatively by chloramine-T in acid solution at room temperature.

From the above discussion, it appears that most of the oxidimetric methods are incorrect, due mainly to the partial conversion of sulphite to dithionate which resists further oxidation. It appeared to us that, if the reactions are carried out in the presence of a suitable catalyst, the dithionate formed can also be oxidized to sulphate. In the investigations reported in this paper, the use of catalysts, with permanganate, ceric sulphate, dichromate, and vanadate has been investigated at varying acid concentrations. With all the oxidants, we have been able to establish conditions of acid concentration and catalyst necessary to secure quantitative oxidation of sulphite to sulphate.

EXPERIMENTAL

The sodium sulphate solution was prepared with water that had been previously boiled to drive off oxygen, and cooled in an atmosphere of carbon dioxide. The solution was preserved in a bottle connected to a burette from which known volumes could be measured out under anaerobic conditions. During the course of an investigation, the sulphite solution was standardised at hourly intervals iodimetrically.

Estimations with potassium permanganate

Almost every investigator has discarded the permanganate method as being impracticable for the estimation of sulphite. From a survey of the literature on the reaction between permanganate and sulphite, it is clear that the chief source of error is a partial conversion of sulphite to dithionate. It appeared possible to us to avoid the formation of dithionate by carrying out the reaction in the presence of a suitable catalyst. In the following experiments we used copper sulphate as catalyst, about 1 ml of 1% copper sulphate being added to about 50 ml of the reaction mixture. The procedure adopted was as follows. A known volume (about 10 ml) of 0.05N permanganate solution was taken in a flask through which carbon dioxide was constantly passed. The catalyst solution was then added and after the requisite quantity of acid was added the solution was diluted to about 40 ml. A known volume of sulphite solution was then run into the mixture and allowed to react for a minute. The excess of permanganate was then determined by treating the mixture with a known excess of standard ferrous ammonium sulphate and the unreacted ferrous sulphate estimated by titration with the same standard permanganate solution. From these experiments, the amount of permanganate required for the oxidation of sulphite was computed and hence the amount of sodium sulphite. The results are given in Table II.

TABLE II

REACTION BETWEEN SODIUM SULPHITE AND POTASSIUM PERMANGANATE

Amount of sodium sulphite taken 0.565 millimols

Concentration of sulphuric acid	*Amount of sulphite found in millimols*	
	without catalyst	*with copper sulphate as catalyst*
0.5 N	0.531	0.560
1.0 N	0.525	0.558
2.0 N	0.525	0.551
3.0 N	0.521	0.541
4.0 N	0.520	0.538

From the above results, it appears that as the concentration of acid is decreased the results approach closer to the theoretical; hence a series of experiments were conducted in a weak acid medium using 1N acetic acid concentration. These gave satisfactory results and therefore a large number of estimations were made in 1N

acetic acid medium using copper sulphate as catalyst. Typical results are given in Table III.

TABLE III

PERMANGANOMETRIC ESTIMATION OF SULPHITE IN ACETIC MEDIUM WITH COPPER SULPHATE AS CATALYST

Amount of sulphite taken (iodometric method) in millimols	*Amount of sulphite found modified $KMnO_4$ method in millimols*	*Error*
0.1275	0.1275	nil
0.2550	0.2550	nil
0.3825	0.3820	0.12%
0.5100	0.5090	0.2%
0.7650	0.7620	0.4%
0.8925	0.8900	0.28%
1.0200	1.0150	0.5%

Use of iodine monochloride catalyst

In the following experiments iodine monochloride has been used as a catalyst with permanganate. The iodine monochloride is prepared by dissolving 0.279 g of potassium iodide and 0.178 g of potassium iodate in 250 ml of water and making up to 500 ml with concentrated hydrochloric acid (sp. gr. 1.18). 1 ml of this solution was used as catalyst per 50 ml of the reaction mixture. Preliminary experiments on the effect of varying sulphuric acid concentration gave the results shown in Table IV.

TABLE IV

REACTION BETWEEN SODIUM SULPHITE AND POTASSIUM PERMANGANATE WITH IODINE MONOCHLORIDE AS CATALYST

Amount of sodium sulphite taken 0.5650 millimols

Concentration of sulphuric acid	*Amount of sodium sulphite found in millimols*	
	without catalyst	*with ICl as catalyst*
0.5*N*	0.5310	0.5650
1.0*N*	0.5250	0.5630
2.0*N*	0.5250	0.5640
3.0*N*	0.5210	0.5650
4.0*N*	0.5200	0.5650

Several estimations have been carried out with permanganate at about 1*N* sulphuric acid concentration with iodine monochloride as catalyst. Some typical results are given in Table V.

TABLE V

ESTIMATION OF SODIUM SULPHITE WITH POTASSIUM PERMANGANATE WITH IODINE MONOCHLORIDE CATALYST

Amount of sulphite taken (iodometric method) in millimols	*Amount of sulphite found in modified permanganate method in millimols*	*Error*
0.1425	0.1425	nil
0.2850	0.2855	0.17%
0.5250	0.5240	0.2%
0.7075	0.7060	0.21%
0.8500	0.8450	0.5%
1.0500	1.0420	0.8%

From the results presented in Tables III and V it is seen that the modified permanganometric methods give results agreeing closely with those of the standard iodometric method.

LANG AND KURTENACKER (*loc. cit*) found that the reaction of ceric sulphate with sulphite is unsuitable for quantitative estimation as it is not possible to avoid the transformation of a high percentage of sulphite into dithionate. We have now investigated the use of ceric sulphate in conjunction with iodine monochloride catalyst at different concentrations of sulphuric acid. We avoided the use of hydrochloric acid, as we found that ceric sulphate interacts with hydrochloric acid at high concentrations if the two are kept together for some time. The results are given in Table VI.

TABLE VI

REACTION OF SULPHITE WITH CERIC SULPHATE

Amount of sulphite taken = 0.515 millimols

Concentration of sulphuric acid	*Amount of sulphite found (in millimols)*	
	without catalyst	*with ICl catalyst*
1.0*N*	0.3750	0.4850
2.0*N*	0.3850	0.4900
4.0*N*	0.4050	0.5050
6.0*N*	0.4150	0.5125
8.0*N*	0.4350	0.5150
10.0*N*	0.4550	0.5145

From these results, it is evident that a high concentration of sulphuric acid is favourable for the complete oxidation of sulphite to sulphate, and that iodine monochloride serves as a good catalyst. Several estimations were therefore made with ceric sulphate and 7.5*N* sulphuric acid, using 1.0 ml of the iodine monochloride catalyst, the details of procedure being otherwise the same as with potassium dichromate described below. The excess ceric sulphate is estimated by titration with standard Mohr's salt solution, using ferroin as indicator. Typical results are given in Table VII.

TABLE VII

ESTIMATION OF SULPHITE WITH CERIC SULPHATE AT 7.5*N* H_2SO_4 WITH IODINE MONOCHLORIDE CATALYST

Amount of sulphite taken in millimols (iodometric method)	*Amount of sulphite found in millimols (modified ceric sulphate method)*	*Error*
0.1290	0.1290	nil
0.2580	0.2580	nil
0.3865	0.3860	0.13%
0.5150	0.5140	0.20%
0.6485	0.6470	0.25%
0.7825	0.7800	0.32%
0.9165	0.9130	0.38%
1.2975	1.2900	0.62%

These results show that the catalyzed ceric sulphate method which we developed gives good results for the estimation of sulphite. It is to be inferred that under the conditions of our method the oxidation of sulphite to dithionate is is completely avoided.

In view of the successful results which we obtained with the catalyzed permanganate and ceric sulphate methods, it seemed to us profitable to carry out an exhaustive investigation of the reaction between dichromate and sulphite. The procedure we adopted is as follows:-

A known volume (5 to 10 ml) of sulphite solution (about 0.05*N*) is run into a known excess (10-15 ml) of *N*/20 dichromate solution, to which are added the requisite amounts of acid and catalyst (1 ml), and this is allowed to stand for a minute. The excess dichromate is then titrated with a standard solution of ferrous ammonium sulphate, using diphenylbenzidine or N-phenyl anthranilic acid as indicator. Diphenylbenzidine cannot be used in experiments where iodine monochloride has been used. In the Table VIII are given the results illustrative of the use of copper sulphate and iodine monochloride catalysts.

TABLE VIII

REACTION BETWEEN SODIUM SULPHITE AND POTASSIUM DICHROMATE

Amount of sulphite taken = 0.515 millimols

Concentration of hydrochloric acid	*Amount of sulphite found in millimols* *without catalyst*	*ICl catalyst*	*copper catalyst*
0.5*N*	0.5750	0.5750	0.5750
1.0*N*	0.5750	0.5750	0.5750
2.0*N*	0.5680	0.5750	0.5750
3.0*N*	0.5600	0.5750	0.5750
4.0*N*	0.5550	0.5750	0.5750
5.0*N*	0.5500	0.5750	0.5750

From the Table VIII it will be noticed that a catalyst is not necessary for securing accurate results with dichromate, provided the concentration of hydrochloric acid is kept at 0.5 to 1.0*N*. At higher acid concentrations, catalysts are necessary. Hence a large number of estimations were carried out at 1.0*N* HCl concentration,without catalyst. Typical results are given in Table IX.

TABLE IX

ESTIMATION OF SULPHITE WITH DICHROMATE AT 1*N* HCL

Amount of sulphite taken (iodometric method) millimols	*Amount of sulphite found (dichromate method) millimols*	*Error*
0.1437	0.1435	0.14%
0.2875	0.2875	nil
0.5750	0.5740	0.18%
0.7190	0.7170	0.3%
0.8625	0.8600	0.3%
1.1500	1.1450	0.45%

In the above experiments, the unreacted dichromate was titrated with standard ferrous ammonium sulphate solution using diphenylbenzidine as indicator. From the results in Table VIII, it is already evident that as the hydrochloric acid concentration increases, errors appear. Estimations were thus carried out at higher HCl concentrations using ICl or copper sulphate as catalyst. When so catalyzed, the reaction yields good results as seen from the Table X.

TABLE X

ESTIMATION OF SULPHITE WITH DICHROMATE WITH ICl AS CATALYST AT $5N$ HYDROCHLORIC ACID

Amount of sulphite taken (iodometric method) millimols	*Amount of sulphite found (catalyzed dichromate method) millimols*	*Error*
0.132	0.1312	nil
0.2625	0.2625	nil
0.3937	0.3930	0.17%
0.5250	0.5240	0.14%
0.7875	0.7860	0.2%
1.0500	1.0450	0.5%
1.3225	1.3050	0.57%

In these experiments, N-phenylanthranilic acid is used as an indicator in the estimation of the unreacted dichromate with standard Mohr's salt solution. Results similar to those in Table X are obtained with dichromate and copper sulphate as catalyst at $5N$ HCl concentration.

Experiments with potassium dichromate in sulphuric acid medium

Table XI incorporates the results obtained when sulphuric acid was used in place of hydrochloric acid under the experimental conditions described in the previous sections.

TABLE XI

REACTION OF SULPHITE WITH POTASSIUM DICHROMATE IN SULPHURIC ACID MEDIUM

Amount of sulphite taken = 0.5650 millimols

Concentration of sulphuric acid	*Amount of sulphite found in millimols*	
	without catalyst	*with ICl catalyst*
$0.1N$	0.5620	0.565
$0.5N$	0.5560	0.565
$1.0N$	0.5500	0.565
$2.0N$	0.5400	0.565
$3.0N$	0.5400	0.565
$4.0N$	0.5380	0.565
$5.0N$	0.5350	0.565

From these results, it will be seen that when the sulphuric acid concentration is increased in the uncatalyzed experiments, the amount of sulphite determined becomes lower and lower than the amount taken. But when the ICl catalyst is employed, values agreeing with the theoretical are obtained at all concentrations of sulphuric acid. A number of estimations have been made on unknown samples in 1N H_2SO_4 medium with ICl catalyst. Some typical results are given in Table XII.

TABLE XII

ESTIMATION OF SULPHITE WITH DICHROMATE IN 1N H_2SO_4 MEDIUM USING ICl CATALYST

Amount of sulphite taken in millimols (iodometric methods)	*Amount of sulphite found in millimols (dichromate method)*	*Error*
0.1412	0.1413	0.07%
0.2825	0.2825	nil
0.4237	0.4230	0.16%
0.5650	0.5640	0.18%
0.8475	0.8460	0.18%
1.1300	1.1230	0.6%

Experiments with potassium dichromate in acetic acid medium

In view of the results obtained in sulphuric and hydrochloric acid media, we also carried out experiments with potassium dichromate as an oxidizing agent in acetic acid medium. It was found that copper salts do not exert any catalytic action when acetic acid is used. Moreover there is no need for any catalyst as even the uncatalysed reaction between sulphurous acid and chromic acid quickly reaches quantitative completion, in 1N to 3N acetic acid media. A large number of determinations of sulphite have been made with chromic acid in a medium acidified with 1.0N acetic acid and Table XIII shows some typical results.

TABLE XIII

ESTIMATION OF SULPHITE WITH POTASSIUM DICHROMATE IN ACETIC ACID MEDIUM

Amount of sulphite taken in millimols (iodometric method)	*Amount of sulphite found in millimols (dichromate method)*	*Error*
0.1450	0.1450	nil
0.2900	0.2900	nil
0.4350	0.4340	0.23%
0.5800	0.5790	0.17%
0.7250	0.7230	0.28%
1.0150	1,0100	0.5%
1.305	1.2980	0.54%

From these results, it is clear that estimations of sulphite with potassium dichromate in acetic acid medium yield accurate results, even without the use of a catalyst.

Estimation of sulphite with vanadate

Lang and Kurtenacker *(loc. cit)* obtained accurate results in the determination of sulphite with vanadic acid using their own method. The sulphite solution to be examined, which should contain not more than about 0.12 g SO_3 (equivalent to 30 ml of 0.1N solution), is run into 20 ml of 0.2N vanadic acid (prepared by adding 25 g of ammonium vanadate to 1:1 sulphuric acid while stirring, and then diluting with water to 1 liter). After about 10 minutes, 30 ml of 10N sulphuric acid are added, and the mixture is heated and kept slowly boiling for 20 minutes. Then the vanadyl salt formed is titrated hot with permanganate to the color change from yellow to violet brown. Care should be taken that the total volume of liquid, after addition of sulphuric acid, does not exceed 100 ml.

It is evident that the method proposed by Lang and Kurtenacker is rather tedious. We managed to work out a much simpler procedure by using iodine monochloride as a catalyst. The sulphite solution is added to a slight excess of sodium vanadate solution containing hydrochloric acid at an overall acid concentration of $5N$ and 1 ml of iodine monochloride catalyst. The mixture is allowed to stand for five minutes and the excess of vanadate titrated with standard Mohr's salt solution, using N-phenylanthranilic acid as indicator. Diphenylbenzidine is not suitable as it gets destroyed. It will be noted that this method has several advantages over that proposed by Lang and Kurtenacker, the chief of which is that the reaction is carried out at room temperature, avoiding the prolonged boiling they prescribe. Typical results culled from a large number of estimations are given in Table XIV.

TABLE XIV

VANADAMETRIC ESTIMATION OF SULPHITE

Amount of sulphite taken (iodometric method)	*Amount of sulphite found (vanadametric method)*	*Error*
0.1340 millimols	0.1340 millimols	nil
0.2675 ,,	0.2675 ,,	nil
0.4015 ,,	0.4010 ,,	0.13%
0.5150 ,,	0.5140 ,,	0.20%
0.6485 ,,	0.6470 ,,	0.25%
0.7825 ,,	0.7800 ,,	0.32%
1.0300 ,,	1.0250 ,,	0.50%
1.2976 ,,	1.2900 ,,	0.62%

We found that copper salts are not very useful as catalysts for the vanadate oxidation of sulphite.

SUMMARY

1. The use of permanganate, ceric sulphate, and dichromate for the estimation of sulphite has been reinvestigated, although these reagents have been discarded as useless by earlier investigators. By using catalysts under controlled acid concentration, we have been able to develop conditions for the quantitative oxidation of sulphite to sulphate at room temperature by any one of these oxidizing agents, avoiding the formation of dithionate. Copper sulphate and iodine monochloride have been found useful as catalysts with potassium permanganate and dichromate; but only iodine monochloride with ceric sulphate.

2. Sodium sulphite is also oxidized quantitatively to sulphate at room temperature, when added to excess of sodium vanadate solution containing 5 to $6N$ hydrochloric acid and iodine monochloride as catalyst.

RÉSUMÉ

1. L'emploi du permanganate, du sulfate de cérium(IV) et du dichromate pour le dosage des sulfites a été examiné à nouveau, bien que ces composés aient été considérés comme inutilisables par certains auteurs. En présence de catalyseurs, à pH contrôlé, on a pu établir les conditions d'oxydation quantitative des sulfites en sulfates, à la température ordinaire, par l'un de ces trois oxydants, sans qu'il y ait formation de dithionate. Le sulfate de cuivre et le monochlorure d'iode conviennent comme catalyseurs dans le cas du permanganate de potassium et du dichromate; tandis que seulement le monochlorure d'iode convient pour le sulfate de cérium(IV).

2. Le sulfite de sodium peut également être oxydé quantitativement en sulfate à la température ordinaire lorsqu'il est ajouté à un excès de vanadate de sodium, renfermant de l'acide chlorhydrique 5 à $6N$ et du monochlorure d'iode, comme catalyseur.

ZUSAMMENFASSUNG

1. Die Verwendung von Permanganat, Cerium(IV) Sulfat und Bichromat für die Bestimmung von Sulfiten ist von neuem untersucht worden, obwohl diese Verbindungen von gewissen Autoren, als unbrauchbar betrachtet worden sind. In Gegenwart von Katalisatoren bei einem kontrollierten

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pH-Wert, konnte man die Bedingungen für die quantitative Oxydation von Sulfiten zu Sulfaten festlegen, bei normaler Temperatur, mit einem dieser drei Oxydationsmittel, ohne Bildung von Dithionat. Das Kupfersulfat und das Jodmonochlorid eignen sich im Falle des Kaliumpermanganates und des Bichromates als Katalisatoren; während nur das Jodmonochlorid sich für das Cerium(IV)-Sulfat eignet.

2. Das Natriumsulfit kann ebenfalls quantitativ zu Sulfat oxydiert werden bei gewöhnlicher Temperatur, wenn man einen Überschuss von Natriumvanadat dazugibt, welches 5-6*N* Salzsäure und Jodmonochlorid als Katalisator enthält.

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OXIDATIONS WITH ALKALINE PERMANGANATE USING MONOVALENT THALLIUM FOR THE BACK TITRATION

I. ESTIMATION OF LEAD, SELENIUM, TELLURIUM AND CHROMIUM

by

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STAMM[1] recommended the use of formate in the back titration of $KMnO_4$ in alkaline media. His method depends on the titration of $KMnO_4$ in presence of Ba^{+2} ions which check the reduction at the manganate state. The end-point is detected by the disappearence of the pink colour through the green $BaMnO_4$ precipitate but the potentiometric estimation of the end-point was preferred to the visual method[2,3]. However, the reaction is not rapid especially near the end-point where it needs ∼10 minutes for the attainment of equilibrium.

Recently a new method for the macro- and microdetermination of thallium, by oxidation with $KMnO_4$ in alkaline media, has been devised[4]. Reduction of $KMnO_4$ with Tl^+ was then tried and the reaction, which was performed under a variety of conditions, proved very suitable in back titrating excess permanganate in the course of several determinations. This reagent is preferred to formic acid on account of the shorter time taken to achieve equilibrium.

TABLE IA

TITRATION OF $KMnO_4$ WITH Tl^+ IN PRESENCE OF Ba^{+2} IONS

Alkalinity	*Max. inflection per 0.1 ml Tl^+*	*mg Tl equiv. to $KMnO_4$*	*mg Tl consumed in titration*	*Error %*
25 ml 0.1261N $KMnO_4$ titrated with 0.088N Tl^+:				
0.5N	152 mV	79.395	81.277	2.37
1N	157 ,,	79.395	79.506	0.14
1.5N	148 ,,	79.395	79.173	—0.28
2N	144 ,,	79.395	78.394	—1.26
10 ml 0.1261N $KMnO_4$ titrated with 0.022N Tl^+:				
1N	125 mV	31.758	31.700	—0.18
1N	120 ,,	31.758	31.729	—0.09
25 ml 0.02522N $KMnO_4$ titrated with 0.0176N Tl^+:				
1N	94 mV	15.879	15.724	—0.98
0.75N	94 ,,	15.879	15.812	—0.42
25 ml 0.02522N $KMnO_4$ titrated with 0.0088N Tl^+:				
1N	62 mV	15.879	15.574	—2.3
0.75N	62 ,,	15.879	15.800	—0.5

EXPERIMENTAL

The experimental procedure and the preparation of solutions are the same as previously described[5].

(A) *Titration of permanganate with monovalent thallium in presence of Ba^{+2} ions*

As is shown below, in the titration of $KMnO_4$ with $Tl+$ in alkaline solutions, reduction of the former yields manganate which undergoes further reduction to MnO_2. However, the reaction could be checked at the manganate state by the addition of Ba^{+2} ions. In this latter case equilibrium is rapidly attained after each addition of titrant, but it takes ∿ 5 minutes at the end-point.

The data shown in Table I indicate that accurate results could be obtained in the case of the concentrated solutions used (0.1261*N* $KMnO_4$ and 0.088*N* $Tl+$) when the solution is made 1—1.5*N* with respect to NaOH and in presence of Ba^{+2} ions sufficient to precipitate all the manganate. At lower and higher alkalinities large errors are observed due to reduction of $KMnO_4$ passing partially to MnO_2 in the former case and to its autodecomposition in the latter.

However, on diluting the permanganate five-fold and keeping the alkalinity at 1*N* NaOH, the end-points are attained somewhat earlier than the theoretical. In this case better results could be obtained by making the solution 0.75*N* with respect to NaOH.

The titration curves (Fig. 1 A) are smooth and characterized by large leaps in potential amounting to 150 mV per 0.1 ml of 0.088*N* $Tl+$, but decrease when the permanganate or the thallous salt concentration is lowered.

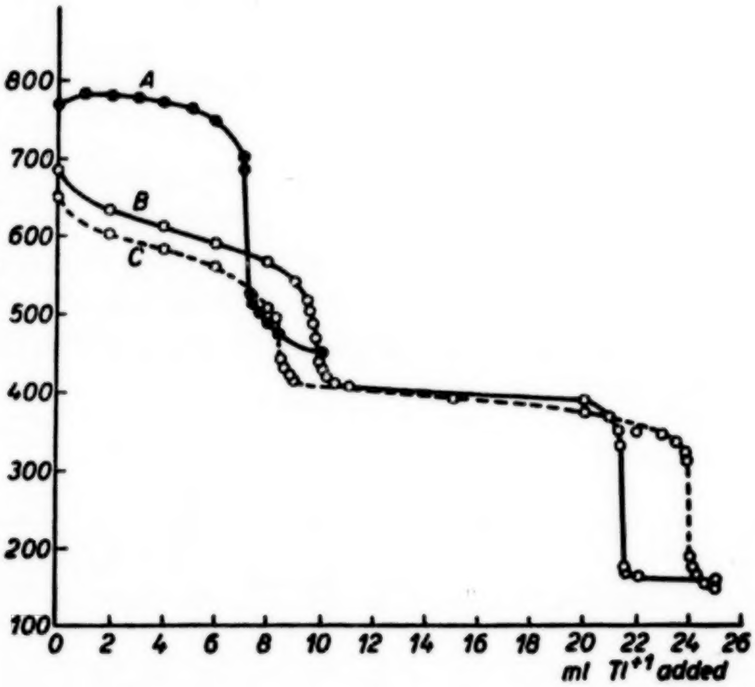

Fig. 1. Titration of 25 ml 0.1261*N* $KMnO_4$ with 0.088*N* $Tl+$
(A) in presence of Ba^{+2} ions and 1*N* NaOH;
(B) in absence of Ba^{+2} ions, in presence of telluric acid and 2.5*N* NaOH;
(C) in absence of Ba^{+2} ions and telluric acid, in presence of 2.5*N* NaOH.

The results also depend on the rate of adding the titrant (see Table I B). Thus, the end-point is attained later than the theoretical value when much $Tl+$ is added first. In order to obtain good results $Tl+$ should be added 1 or 2 ml at a time.

TABLE IB

TITRATION OF 10 ml 0.1261*N* $KMnO_4$ IN 1*N* NaOH IN PRESENCE OF Ba^{+2} IONS WITH 0.0368*N* $Tl+$

ml Tl^+ added	*Max. inflec. per 0.1 ml Tl^+*	*Theoretical end-point*	*Experimental end-point*	*Error %*
1 ml at a time	109 mV	6.853 ml	6.866 ml	0.20
2 ml at a time	110 ,,	6.853 ,,	6.868 ,,	0.22
4 ml 1st	106 ,,	6.853 ,,	6.943 ,,	1.31
6 ml 1st	98 ,,	6.853 ,,	7.063 ,,	3.07

(B) *Titration of permanganate with monovalent thallium in absence of Ba^{+2} ions*

In absence of Ba^{+2} ions reduction of $KMnO_4$ leads primarily to the formation of manganate which then passes to MnO_2. The titration curves (Fig. 1 B and C) are characterized by two inflections,

one occurring at the manganate, the other at the MnO_2 state. In both cases the end-point is attained later than the theoretical value due apparently to the reduction partially passing to MnO_2 at the manganate state and perhaps to Mn_2O_3 at the MnO_2 stage. With the more concentrated solutions used the errors are considerable, but decrease especially at the manganite state by lowering the concentration of Tl^+, such that in case of $8.8 \cdot 10^{-3} N$ Tl^+ the error amounts only to 1%. The reaction occurs rapidly at the beginning of the titration but slows after the first inflection, needing ∼ 5 minutes at first and 15 minutes near the end-point.

TABLE II

TITRATION OF $KMnO_4$ WITH Tl^+ IN ABSENCE OF Ba^{+2} IONS

Alkalinity	*Max. inflec.*		*Theoretical end-point, ml*		*Exp. end-point ml*		*Error %*	
	Mn^{+6}	*Mn^{+4}*	*Mn^{+6}*	*Mn^{+4}*	*Mn^{+6}*	*Mn^{+4}*	*Mn^{+6}*	*Mn^{+4}*
25 ml 0.1261*N* $KMnO_4$ titrated with 0.088*N* Tl^+:								
2.5*N*	32 mV	121 mV	7.16	21.49	10.44	23.97	45.25	11.44
3*N*	25 ,,	105 ,,	7.16	21.49	10.15	23.66	40.66	10.09
25 ml 0.02552*N* $KMnO_4$ titrated with 0.0176*N* Tl^+:								
2*N*	19 mV	85 mV	7.15	21.49	9.74	22.25	36.03	3.33
12.5 ml 0.02552*N* $KMnO_4$ titrated with 0.0088*N* Tl^+:								
2*N*	32 mV	62 mV	7.16	21.49	8.96	21.73	25.14	1.12

If the errors observed at the manganite state, are due to partial formation of Mn_2O_3, then it is possible to obtain better results by performing the titrations in presence of telluric acid. Telluric acid gives rise to a soluble complex[6] with quadrivalent manganese and by the virtue of this property may prevent the reduction of manganese below the manganite state. Under these conditions reduction of $KMnO_4$ still passes from the early stages to Mn^{+4} (as is apparent from the late end-points corresponding to manganate) but the second inflection (occurring at the manganite state) coincides with the theoretical value. As is clear from the data shown in Table III, the errors amount on the average to ∼ 0.3%. Equilibria are rapidly attained when the process consists in the reduction of Mn^{+7} to Mn^{+6}, but need longer when the reaction involves the reduction of Mn^{+6} to Mn^{+4}. In this latter case it takes ∼ 5 minutes beyond the first inflection and 8-10 minutes at the end-point. The reaction involving reduction of MnO_4^- to MnO_4^{-2} in presence of Ba^{+2} ions is, however, more suitable with regard to the rapidity of attaining equilibria.

TABLE III

TITRATION OF $KMnO_4$ WITH Tl^+ IN PRESENCE OF TELLURIC ACID

Alkalinity	*Max. inflec. per 0.1 ml Tl*		*Theor. end-point ml*		*Exp. end-point ml*		*Error %*	
	Mn^{+6}	*Mn^{+4}*	*Mn^{+6}*	*Mn^{+4}*	*Mn^{+6}*	*Mn^{+4}*	*Mn^{+6}*	*Mn^{+4}*
25 ml 0.1261*N* $KMnO_4$ titrated with 0.088*N* Tl^+:								
1*N*	30 mV	138 mV	7.16	21.49	10.93	21.44	52.7	—0.33
2.5*N*	32 ,,	161 ,,	7.16	21.49	9.83	21.43	37.3	—0.28
10 ml 0.1261*N* $KMnO_4$ titrated with 0.0369*N* Tl^+:								
3*N*	76 mV	143 mV	2.4	7.2	3.15	7.14	31.25	—0.83
5*N*	71 ,,	96 ,,	2.4	7.2	2.85	6.97	18.75	—3.19
5*N*	61 ,,	104 ,,	2.4	7.2	3.06	6.94	27.5	—3.61
10 ml 0.1261*N* $KMnO_4$ titrated with 0.088*N* Tl^+:								
2*N*	34 mV	69 mV	11.46	34.39	12.46	34.27	8.7	—0.35
25 ml 0.01261*N* $KMnO_4$ titrated with 0.0176*N* Tl^+:								
1.5*N*	27 mV	51 mV	7.16	21.49	7.75	21.37	6.8	—0.55

(C) *Application of monovalent thallium for the estimation of Te^{+4}, Se^{+4}, Pb^{+2}, and Cr^{+3}*

The methods previously used for the estimation of Pb^{+2}, Se^{+4}, Te^{+4} and Cr^{+3} depend upon mixing their solutions with $KMnO_4$ made 1N or 2N with respect to NaOH, in presence or absence of Ba^{+2} ions respectively. The excess of $KMnO_4$ is then back titrated with formic acid (in presence of Ba^{+2} ions). In this investigation the same procedure was applied, but formic acid is substituted with monovalent thallium both in the presence or absence of Ba^{+2} ions. This reagent was preferred on account of the rapidity of its reaction with $KMnO_4$; the titration needing only half the time taken with formic acid. Tl^+ is a stronger reducing agent than formate, and there is some risk that reduction of $KMnO_4$ in presence of Ba^{+2} ions might proceed partially to MnO_2. Good results can however be obtained provided that addition of Tl^+ is made slowly. This is apparent from the data shown in Table IV which contains results obtained on back titrating excess $KMnO_4$ in presence of Ba^{+2} ions and 1N NaOH.

TABLE IV

NORMALITY OF Tl^+ USED FOR TITRATION = 0.0368N

Vol. & Normality of $KMnO_4$	*Vol. & Normality of solution added*		*Amount added in mg*	*Amount found in mg*	*Error %*
25 ml 0.1246N	5 ml 0.0601N	Pb^{+2}	31.133	31.026	—0.34
25 ml 0.1246N	25 ml 0.1815N	Se^{+4}	17.941	17.441	—0.21
25 ml 0.1246N	3 ml 0.0714N	Te^{+4}	15.198	15.242	0.29
10 ml 0.1261N	1 ml 0.1127N	Cr^{+3}	1.934	1.938	0.26
10 ml 0.1261N	0.5 ml 0.01202N	Pb^{+2}	0.623	0.626	0.48
10 ml 0.1261N	0.5 ml 0.01N	Te^{+4}	0.319	0.318	—0.31
10 ml 0.1261N	1 ml 0.0376N	Cr^{+3}	0.645	0.642	—0.46
20 ml 0.1261N	5 ml 0.00454N	Se^{+4}	0.899	0.894	—0.56

RESULTS

TABLE V

NORMALITY OF $KMnO_4$ = 0.1153N NORMALITY OF Tl^+ = 0.029

Vol. of $KMnO_4$	*Vol. & Normality of solution added*		*Amount added in mg*	*Amount found in mg*	*Error %*
5 ml	0.5 ml 0.1202N	Pb^{+2}	6.227	6.217	—0.16
5 ,,	0.5 ml 0.01202N	Pb^{+2}	0.623	0.621	—0.32
5 ,,	0.5 ml 0.00454N	Se^{+4}	0.899	0.897	—0.22
5 ,,	2 ml 0.0425N	Te^{+4}	5.768	5.787	0.33
2.5 ,,	0.5 ml 0.01N	Te^{+4}	0.319	0.321	0.64
10 ,,	10 ml 0.0425N	Te^{+4}	28.840	28.771	—0.24
10 ,,	2 ml 0.1160N	Cr^{+3}	2.022	2.061	0.19

In Table V are listed the results obtained when the titrations are performed in the presence of telluric acid whence reduction of MnO_4^- passes to Mn^{+4}. Reactions performed under these conditions possess several advantages in that the end-point is independent of (a) the alkali concentration (b) the rate of adding the solution containing the substance to be estimated or its amount, provided that it does not exceed the amount of $KMnO_4$ present, and (c) the rate of adding the monovalent thallium in back titrations as reduction is not overstepped below the manganite state in presence of telluric acid.

SUMMARY

Monovalent thallium can be successfully used for the back titration of $KMnO_4$ in the course of estimating Pb^{+2}, Se^{+4}, Te^{+4} and Cr^{+3}.

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Reduction of $KMnO_4$ with Tl^+ in alkaline solution yields MnO_4^{-2} which then passes to MnO_2. The end-points are attained late, but in presence of telluric acid the end-point at MnO_2 stage corresponds to the theoretical value. Reduction at the MnO_4^{-2} stage can be checked in presence of Ba^{+2} ons and good results obtained with 1-1.5*N* NaOH.

RÉSUMÉ

Le thallium(I) peut être utilisé avec succès pour déterminer l'excès de $KMnO_4$ lors des titrations de Pb^{+2}, Se^{+4}, Te^{+4} et Cr^{+3}. La réduction de $KMnO_4$ par Tl^+, en solution alcaline, conduit à MnO_4^{-2}, puis à MnO_2. Les points finals sont retardés, mais en présence d'acide tellurique, ils correspondent (au stade MnO_2) aux valeurs théoriques. La réduction en manganate a lieu en présence d'ions Ba^{+2}; les résultats obtenus dans NaOH 1-1.5*N* sont bons.

ZUSAMMENFASSUNG

Das einwertige Thallium kann mit Erfolg für die Titration des Überschusses an $KMnO_4$, während der Bestimmung von Pb^{+2}, Se^{+4}, Te^{+4}, und Cr^{+3} verwendet werden.

Die Reduktion von $KMnO_4$ mit Tl^+ in alkalischen Lösungen gibt MnO_4^{-2}, welches dann in MnO_2 übergeht. Die Endpunkte liegen höher als es dem theoretischen Wert des Endpunktes der MnO_2 Stufe entsprechen würde. Die Reduktion kann in Anwesenheit von Ba^{+2} Ionen an der Manganat Stufe zur Ende gebracht werden. Die erhältenen Ergebnisse in 1-1.5*N* NaOH sind befriedigend.

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ANALYTICAL APPLICATIONS OF THE PHOTOCHEMICAL ACTION OF LIGHT

I. DETERMINATION OF FERRIC IRON BY PHOTOCHEMICAL REDUCTION IN THE PRESENCE OF CITRIC AND MANDELIC ACIDS

by

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It is well known that visible and ultra-violet light accelerate many chemical reactions slow to occur in the dark. The action of light is not merely catalytic; whereas catalysts only alter the speed of reactions accompanied by a free energy decrease, light can bring about the acceleration of two thermodynamically distinct types of reactions, namely those accompanied by a free energy increase and those accompanied by a free energy decrease. The profound influence light exerts on the speed of chemical reactions can give rise to important analytical applications. In view of this fact it is surprising that the chemical action of light has not received the attention deserved from analytical chemists.

Light has been used hitherto only in a few instances to increase the speed of reactions so that they may serve as basis for quantitative determinations. The official method for the determination of ergotoxine is based on a photochemical reaction. From a 1 ml sample, the ergotoxine is extracted as ergotoxine ethane sulphonate. The extract, treated with 2 ml of a solution of *para*-dimethylamino benzaldehyde in a mixture of sulphuric acid and water is warmed at 45° C and then exposed to bright light for a period varying from 10 minutes to two hours, according to the intensity of the radiation. The blue colour developed is then measured against standards.

A similar method developed by SPIES AND CHAMBERS[1] for the determination of tryptophane involved condensation with *p*-dimethylamino benzaldehyde in 10N sulphuric acid. The colourless product was then exposed to light for 20 minutes and the intensity of the blue colour developed measured after completing the oxidation by the addition of sodium nitrite.

The reaction between methylene blue and ascorbic acid is quite slow in the dark, but is greatly accelerated by exposure to sunlight or artificial light. MARTINI AND BONSIGNORE[2] were the first to apply this photochemical reaction to the determination of ascorbic acid. LUND AND LIECK[3], LUND AND TRIER[4] and WILAND[5] have also investigated this method. BONSIGNORE AND BEVILAQUA[6] have studied the effect of pH on the kinetics of the reaction.

GOPALA RAO AND RAMACHARLU[7] employed the photochemical reaction between mercuric chloride and sodium oxalate in the titrimetric determination of mercuric chloride employing uranyl nitrate or ferric chloride as photo-sensitizers for this reaction. They prescribed conditions under which the photochemical reduction to mercurous chloride proceeded quantitatively. The mercurous chloride formed was determined iodometrically.

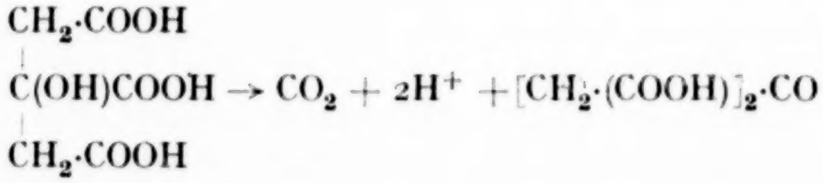
Gopala Rao and Madhusudhana Rao[8] found that when ferric sulphate in dilute sulphuric acid solution was exposed to sunlight in the presence of oxalic acid it was rapidly reduced to the ferrous state which could then be determined by titration with a standard solution of sodium vanadate. This rapid photoreaction thus provided an accurate and easy method for the determination of ferric salts.

In the present investigation, we studied the photochemical reduction of ferric iron in the presence of both citric and mandelic acids with regard to the analytical applications.

The photochemical reduction of ferric salts in the presence of citric acid

Winther and Howe[9] made a study of the photochemical decomposition of ferric oxalate, tartrate and citrate by ultra-violet light. Benrath[10] noted that ferric citrate decomposed into acetone and carbon dioxide as the final products. Acetone dicarboxylic acid and acetoacetic acid were reported as intermediate products. Euler and Ryd[11], Ciamician and Silber[12] also recorded the formation of acetone and carbon dioxide. Fry and Gerve[13] studied the reaction in sunlight and in ultra-violet light taking citric acid in excess and varying the concentration of ferric sulphate. They found that three molecules of carbon dioxide were formed for every molecule of ferric sulphate present. Burt[14] made a study of the same reaction in sunlight and reached similar conclusions. Peltz and Lyman[15] found that citric acid was partially oxidized by ferric hydroxide in sunlight, yielding carbon dioxide and a soluble ferrous salt. Alkali citrates did not decompose under the same conditions. They could not detect any acetone in the exposed solutions. Scoville[16] observed that amber bottles inhibited the reduction of ferric salts of citric, lactic and tartaric acids.

The initial photochemical change of citric acid in the presence of ferric sulphate would appear to be a decomposition into acetone dicarboxylic acid with the elimination of a molecule of carbon dioxide and two hydrogen ions. This may be represented by the equation:



$$\begin{array}{l} CH_2{\cdot}COOH \\ | \\ C(OH)COOH \rightarrow CO_2 + 2H^+ + [CH_2{\cdot}(COOH)]_2{\cdot}CO \\ | \\ CH_2{\cdot}COOH \end{array} \quad \ldots\ldots\ldots\ldots \quad (1)$$

The instability of acetone dicarboxylic acid would lead immediately to the formation of acetoacetic acid and carbon dioxide, according to the equation:

$$[CH_2{\cdot}(COOH)]_2{\cdot}CO \rightarrow CO_2 + CH_3CO \cdot CH_2 \cdot COOH \quad \ldots\ldots\ldots \quad (2)$$

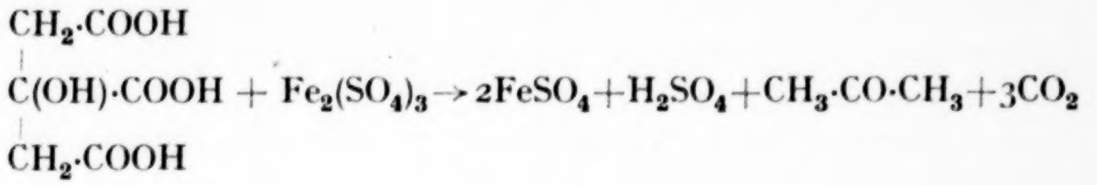
The acetoacetic acid thus formed decomposing into acetone and carbon dioxide as shown below:

$$CH_3 \cdot CO \cdot CH_2 \cdot COOH \rightarrow CH_3 \cdot CO \cdot CH_3 + CO_2 \quad \ldots\ldots\ldots \quad (3)$$

The ferric sulphate may be regarded as interacting with the two atoms of hydrogen formed in equation (1).

$$Fe_2(SO_4)_3 + 2H^+ \rightarrow 2\,FeSO_4 + H_2SO_4 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

Summation of equations (1), (2), (3) and (4) would give



$$\begin{array}{l} CH_2\cdot COOH \\ \mid \\ C(OH)\cdot COOH + Fe_2(SO_4)_3 \rightarrow 2FeSO_4 + H_2SO_4 + CH_3\cdot CO\cdot CH_3 + 3CO_2 \\ \mid \\ CH_2\cdot COOH \end{array} \quad (5)$$

EXPERIMENTAL

Reagents

A $0.0552N$ solution of ferric alum was prepared using Merck's analytical reagent grade ferric alum adding enough A.R. sulphuric acid to make the solution $1.25N$ with respect to sulphuric acid.

(2) A $0.2M$ solution of citric acid was made from pure citric acid supplied by British Drug House Ltd.

(3) A standard solution ($0.05N$) of sodium vanadate was prepared from A.R. ammonium vanadate supplied by British Drug House Ltd.

Procedure

A measured volume of the ferric alum solution mixed with excess of citric acid solution was exposed to light for a suitable time. The photochemical sources of energy employed were sunlight, and light from a 1000 watt tungsten filament lamp. After exposure, the ferrous iron formed by photochemical reduction was determined by titration with standard sodium vanadate using diphenylbenzidine or diphenylamine sulphonic acid as internal indicators. Before titration, 10 ml of syrupy phosphoric acid were added, diluting suitably so that the mineral acid concentration of the solution would not be above $1.0N$.

Potassium dichromate solution cannot be employed in this titration because of interference from unreacted citric acid. The reaction between ferrous iron and dichromate induces the reaction between citric acid and dichromate. LYONS AND APPLEYARD[17] reported that ferrous iron could be determined in presence of citric acid by titration with a standard solution of ceric sulphate, using N-phenylanthranilic acid as indicator. THIRY[18] also recommended the use of ceric sulphate for determining ferrous iron in the presence of citric acid. We found that ceric sulphate is unsuitable for titration of ferrous iron formed in our photochemical experiments as the indicators ferroin and N-phenylanthranilic acid did not respond by giving the colour change at the equivalence point. The colour change could not be obtained even when a large excess of ceric sulphate was added. Obviously the photochemical oxidation products of citric acid interfere in the determination, although according to LYONS AND APPLEYARD (*loc. cit.*) and THIRY citric acid itself does not interfere.

The results in the following table show that ferric iron is quantitatively reduced to the ferrous state when exposed to sunlight in the presence of sufficient citric acid and with a sulphuric acid concentration of $0.25N$.

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The reaction mixture consisted of 10 ml of 0.0552*N* ferric alum + 10 ml of 0.2*M* citric acid solution, diluted to 50 ml and exposed in a quartz beaker to sunlight.

TABLE I

Amount of ferric salt taken = 0.552 milligram equivalent

Time of exposure to sunlight	*Amount of ferric salt reduced, in mg equiv.*
30 minutes	0.4617
60 ,,	0.5520
90 ,,	0.5526

In the following experiments the concentration of citric acid was varied.

10 ml of ferric alum solution (0.0552) + *X* ml of citric acid solution were diluted to 50 ml. The mineral acid concentration was 0.25*N*.

TABLE II

Amount of ferric alum taken = 0.552 mg equivalent

Time	*Overall concn. of citric acid*	*Amount of ferric alum reduced, in mg equiv.*
30 minutes	0.01*M*	0.1795
	0.02 ,,	0.3259
	0.04 ,,	0.4617
	0.08 ,,	0.5138
60 ,,	0.01 ,,	0.2565
	0.02 ,,	0.4617
	0.04 ,,	0.5520
	0.08 ,,	0.5524
90 ,,	0.01 ,,	0.3591
	0.02 ,,	0.5130
	0.04 ,,	0.5521
	0.08 ,,	0.5526
120 ,,	0.02 ,,	0.5520
	0.04 ,,	0.5524

The above results show that as the concentration of citric acid was increased, the amount of ferric iron reduced in a given interval of time was also increased. In other words, quantitative reduction of ferric alum could be secured in a shorter time using a higher concentration of citric acid.

Experiments indicated that increasing the concentration of mineral acid decreased the speed of reduction. Hence the following experiments were conducted in the absence of free mineral acid. The acid in the ferric alum solution was carefully neutralized by sodium hydroxide and then mixed with the citric acid solution. It was found that under these circumstances, the speed of the reduction was not increased by increasing the concentration of citric acid beyond 0.2*M*.

TABLE III

Amount of ferric salt taken = 0.552 mg equivalent
Time of exposure = 30 minutes

Overall concentration of citric acid	*Amount of ferric salt reduced, in mg equiv.*
0.01*M*	0.5517
0.02*M*	0.5520
0.04*M*	0.5520
0.08*M*	0.5520

The results show that quantitative reduction of ferric alum was secured in 30 minutes exposure to sunlight with a citric acid concentration of $0.02M$, the ferric iron concentration being $0.011N$. The reduction was found to be equally effective using either quartz or pyrex glass beakers. Reduction speed was slow in experiments carried out with 1000 watt tungsten filament lamp as the light source.

Photoreduction of ferric salts in the presence of mandelic acid

Preliminary experiments showed that the photochemical reduction of ferric iron by mandelic acid was greatly retarded by sulphuric acid. Hence in our experiments, the sulphuric acid in the ferric alum solution was made almost neutral with sodium hydroxide solution, then mixed with the mandelic acid and exposed to sunlight in a quartz beaker for a suitable length of time, after which the reduced iron was titrated with a standard solution of sodium vanadate, adding sufficient sulphuric and phosphoric acids.

TABLE IV

In these experiments 10 ml of $0.0552N$ ferric alum solution + X ml of $0.09M$ mandelic acid solution were diluted to 50 ml. Amount of ferric alum taken = 0.5520 mg equivalent

Time	*Overall concn. of mandelic acid*	*Amount of ferric alum reduced, in mg equiv.*
15 minutes	$0.009\ M$	0.4930
	0.018 ,,	0.5520
	0.027 ,,	0.5520
30 ,,	0.009 ,,	0.5440
	0.018 ,,	0.5520
	0.027 ,,	0.5520
60 ,,	0.009 ,,	0.5520
	0.018 ,,	0.5521
	0.027 ,,	0.5521

TABLE V

Amount of ferric iron taken = 0.552 mg equivalents

Time of exposure to a 1000-watt	*Overall concn. of mandelic acid*	*Amount of ferric iron reduced in mg equiv.*
60 minutes	$0.009\ M$	0.4027
	0.018 ,,	0.4580
	0.027 ,,	0.5416
	0.036 ,,	0.5495
	0.045 ,,	0.5526
90 ,,	0.009 ,,	0.4879
	0.018 ,,	0.5528
	0.027 ,,	0.5521
	0.036 ,,	0.5521
	0.045 ,,	0.5524
120 ,,	0.009 ,,	0.5338
	0.018 ,,	0.5520
	0.045 ,,	0.5526
150 ,,	0.009 ,,	0.5522
	0.045 ,,	0.5524

It is observed from the above results that quantitative reduction of the ferric salt is secured in 15 minutes if the concentration of mandelic acid is $0.018M$. The reduction was found to proceed with equal facility either in quartz or glass beakers. It was found that although the reaction was slower in the light from a 1000 watt tungsten filament lamp than in sunlight, the reduction could still be completed in 90 minutes under suitable conditions. In the following experiments, the mixture was irradiated by a 1000 watt lamp running on 220 volts A.C. mains. The level of the liquid was kept 6 inches below the lamp.

The reaction mixture consisted of 10 ml of nearly neutral ferric alum solution (0.0552 N) + X ml of mandelic acid ($0.09M$), diluted to 50 ml.

In experiments on the photoreduction of ferric salt by mandelic acid, we found that ceric sulphate can also be used for the titration of ferrous iron using diphenylamine, diphenylbenzidine, or N-phenylanthranilic acid as indicators, provided the proper sulphuric and phosphoric acid concentration is maintained. With ferroin, the difficulty was that the colour change was reversed at the end point, after keeping for about 30 seconds.

SUMMARY

A new method has been developed for the determination of ferric sulphate through its photochemical reduction with citric and mandelic acids in sunlight. The method consists in irradiating with sunlight a measured volume of the ferric sulphate solution together with an excess of citric or mandelic acid in a quartz or pyrex glass beaker until reduction is complete. The ferrous salt formed is determined by titration with a standard solution of sodium vanadate in the presence of the proper concentration of sulphuric and phosphoric acids, employing diphenylbenzidine or diphenylamine sulphonate as internal indicators. The photoreduction is greatly retarded by sulphuric acid.

RÉSUMÉ

Une nouvelle méthode est développée pour le dosage du sulfate de fer(III) par réduction photochimique au moyen des acides citrique et mandélique. Cette méthode consiste à exposer à la lumière solaire, une solution de sulfate de fer(III) (volume connu) en présence d'un excès d'acides citrique et mandélique, dans un bécher de quartz ou de pyrex, pendant environ 30 minutes jusqu'à réduction totale. Le fer(II) formé est titré au moyen d'une solution étalon de vanadate de sodium, en présence des acides sulfurique et phosphorique; on utilise comme indicateur la diphényl-benzidine ou un diphénylamine sulfonate. La photoréduction est considérablement retardée par l'acide sulfurique.

ZUSAMMENFASSUNG

Es wurde eine neue Methode entwickelt um Eisen(III)-sulfat mittels einer photochemischen Reduktion mit Zitronen- und Mandelsäure am Sonnenlicht zu bestimmen. Diese Methode besteht darin eine Eisen(III)-sulfat-Lösung (Volumen bekannt) in Gegenwart eines überschusses von Zitronen- und Mandelsäure in einem Quarz- oder Pyrex Becherglas, während *ca.* 30 Minuten dem Sonnenlicht bis zur vollständigen Reduktion auszusetzen. Das gebildete Eisen(II) wird mit einer Natriumvanadat-Vergleichslösung in Gegenwart von Schwefel- und Phosphorsäure titriert. Als Indikator verwendet man das Diphenylbenzidin oder ein Diphenylaminsulfonat. Die Photoreduktion wird beträchtlich verlangsamt durch die Schwefelsäure.

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RESORCYLALDOXIME AS AN ORGANIC REAGENT

by

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INTRODUCTION

Various organic substances have been employed for the gravimetric determination of copper and nickel and their separation from other elements. FEIGL[1] described the use of α-benzoinoxime for the gravimetric determination of copper in different alloys. The aliphatic acidic grouping, $>C(OH)\text{-}C=NOH\text{-}$, which is the copper specific group of acyloin oximes[2], is responsible for the insolubility and the colour of their copper compounds. EPHRAIM[3,4] introduced the use of salicylaldoxime for the detection and determination of copper. He also studied the reactions of a number of compounds containing the same reactive grouping as salicylaldoxime. Hydrogen ion concentration is an important factor in the use of salicylaldoxime as an analytical reagent[5]. It has been observed that by controlling the pH of the solution, different elements can be detected and determined in the presence of each other by the use of this reagent[6].

During the systematic investigation of the condensation products formed by the interaction of resorcylaldehyde with different amino-acids and related compounds[7], it was observed that resorcylaldehyde in those compounds could be determined gravimetrically as copper or nickel-resorcylaldoximes. As a result of investigations with resorcylaldehyde and its oxime, it has now been observed that resorcylaldoxime can be used conveniently as an organic reagent for copper and nickel. Resorcylaldoxime has only been used for the detection and determination of iron[8]. A search of the literature did not reveal the use of this compound as a gravimetric reagent for copper or nickel. The reagent was easily prepared, following the method described by ASTIN AND RILEY[9] for salicylaldoxime reagent.

The complex copper and nickel compounds were prepared in the pure state and their properties studied. Copper resorcylaldoxime is precipitated completely, even in fairly acid solution, ($pH > 1.40$). The precipitation of nickel resorcylaldoxime begins at pH 4.2 and is quantitative between pH 5.54 and 6.55. Resorcylaldoxime does not give any precipitate with cadmium or zinc even in alkaline solution. Cobalt gives no precipitate in acid solution, but in alkaline solution it gives a blood-red coloration. Uranium (VI), manganese and lead also give colorations at different pH values, but the reactions are not very sensitive. Copper and nickel, however, could not be separated by this reagent, as copper was always found to give a low results in the presence of nickel.

The complex salts of copper and nickel are stable, insoluble in water, and dilute acetic acid, and could be weighed in sintered glass gooch crucibles after drying at 95-100° C for one hour.

The copper and nickel complexes have the composition, $Cu(C_7H_6O_3N)_2$ and $Ni(C_7H_6O_3N)_2$, respectively. The conversion factor for copper is 0.1729 and for nickel, 0.1618. A distinct opalescence is observed with solutions containing 1 part of copper per 40,000 part or 1 part of nickel per 200,000 part; 0.25 p.p.m. of nickel gives a distinct coloration. Like salicylaldoxime, resorcylaldoxime has been successfully used for the direct determination of copper in brass. The reagent has some advantages over several known methods. Resorcylaldoxime is quite stable and could be preserved for long periods. From magnetic moment measurements on the complexes formed, it can be concluded that copper and nickel resorcylaldoxime compounds are penetration complexes with planar dsp^2 hybrid bonds.

EXPERIMENTAL

Reagent. Resorcylaldoxime was prepared according to the method of MARCUS[10]. Freshly prepared 1-2% solution of resorcylaldoxime (m.p. 198-99° C) were used in this work. The reagent solution (approximately 1%) could also be prepared by following the method employed by ASTIN AND RILEY *(loc. cit.)* for salicylaldoxime. 1.25 g of resorcylaldehyde was dissolved in the minimum amount (5 ml) of alcohol and 0.75 g of hydroxylamine hydrochloride (in 5 ml water) added. The resulting mixture was thoroughly shaken, 5 ml absolute alcohol was added to it, and the volume made up to 100 ml with water. This solution can be readily prepared during the process of estimation.

Copper and Nickel complexes. (a) Copper-resorcylaldoxime was obtained by the interaction of copper acetate (1 mol) and resorcylaldoxime (2 mol) in aqueous alcoholic medium (between pH 2.15 and 3.5). The greenish-grey precipitate was then filtered, washed with cold water and a small quantity of alcohol, and finally dried over concentrated sulphuric acid. The compound is insoluble in cold and hot water, as well as in dilute acetic acid, chloroform, benzene and toluene but soluble in acetone, dioxane, pyridine and absolute alcohol. The compound loses one molecule of water at 90-95° C.

[Found: Cu, 16.51; N, 7.10; C, 43.62; H, 3.05 and H_2O, 4.63%: $Cu(HO.C_6H_3O.CH = NOH)_2.H_2O$ requires Cu, 16.49; N, 7.25; C, 43.56; H, 3.60 and H_2O, 4.66%.]

(b) Nickel-resorcylaldoxime: Nickel acetate (1 mol) and resorcylaldoxime (2 mol) reacted in aqueous alcoholic medium to give a light green precipitate. The precipitate washed first with water and then with a small amount of alcohol, was finally dried *in vacuo* over concentrated sulphuric acid.

The compound is insoluble in hot as well as in cold water, and also in benzene, chloroform and toluene, but is fairly soluble in dioxane, acetone and pyridine. [Found: Ni, 15.39 and N, 7.33%. $Ni(OH.C_6H_3O.CH = NOH)_2.H_2O$ requires Ni, 15.42 and N, 7.34%.]

Magnetic measurements. The magnetic susceptibilities of the copper and nickel compounds were measured, using a Gouy balance in a magnetic field of strength $9.02 \cdot 10^3$ gauss, and taking all the necessary precautions[11]. The results of the measurements at 30° C are tabulated below:

	$\chi_g \cdot 10^{-6}$	$\chi_m \cdot 10^{-6}$	$\chi_m \cdot 10^{-6}$ (corr.)	μB (effective)
Copper-resorcylaldoxime	3.358	1295	1360	1.73
Nickel-resorcylaldoxime	−0.1046	....	....	Diamagnetic

Solutions and apparatus. Standard copper and nickel solutions were prepared by dissolving E. Merck's reagent quality copper chloride or copper sulphate and nickel chloride respectively in distilled water. The copper concentration in the solutions was determined iodometrically. The strength of nickel solution was determined by precipitation with dimethylglyoxime. Solutions of other metal ions were obtained by dissolving their salts (C.P.) in distilled water.

All pH measurements were made using a Cambridge pH meter (Bench type). Sintered glass gooch crucibles (Jena No. 4) were used for filtration, drying, and weighing of the copper and nickel precipitates.

Reactions with different metal ions

CHIEN AND SHIH (*loc. cit.*) reported that resorcylaldoxime gave a purple colour with slightly acid solutions of ferric iron. The reagent, however, gave no coloration with ferrous iron. In the present investigation it was observed that resorcylaldoxime gave precipitates or colours with the following ions at controlled pH:

TABLE I

Ion	*Colour or ppt.*	*pH approx*
Cu^{+2}	ppt.	< 1.05
Ni^{+2}	ppt.	4.2
Mn^{+2}	ppt.	8.6
Hg^{+2}	ppt.	6.5
Co^{+2}	red-colour.	> 7.5
UO_2^{+2}	orange-colour.	> 8

The reagent had no action on Al^{+3}, Sn^{+2}, Zn^{+2}, Cd^{+2}, Cr^{+3}, Ag^{+}, VO_3^{-} or Ce^{+4} ions.

Determination of copper

(i) *Procedure.* The copper solution in a 250 ml Jena beaker was made up to 125 ml and to this 20-25 ml of reagent solution (1%) was added, and then the necessary amount of alkali or sodium acetate solution to maintain the proper pH of 1.8 to 2.85. The mixture was warmed slightly on the water bath, kept for 1/2-1 hour, filtered through a weighed gooch crucible, and washed several times with cold water. The precipitate was dried at 100-105° C for one hour, cooled and weighed. Some representative results are recorded in Table II: (Factor for copper is 0.1729).

TABLE II

'Cu' taken in g	*Wt of 'Cu' ppt. in g*	*'Cu' found in g*
0.00518	0.0302	0.00521
0.01358	0.0784	0.01356
0.02589	0.1493	0.02581
0.03366	0.1946	0.03364
0.03625	0.2095	0.03622

(ii) *Effect of the concentration of the reagent.* The precipitation of copper resorcylaldoxime depends on the amount of reagent present in solution. It was found that precipitation of copper was complete only in the presence of large excess of reagent, (at least 6-7 times by weight). It was noted that best results were obtained using 15-25 ml of a 1% reagent solution for the determination of 4 mg of copper. This is evident from Table III.

TABLE III

Cu^{+2} taken: 0.003827 g and pH of the solution: 1.8-2.2

Reagent taken in g	Reagent required theoretically in g	Wt of 'Cu' ppt. in g	'Cu' found in g
0.05	0.01865	0.0209	0.003612
0.09	0.01865	0.0215	0.003716
0.12	0.01865	0.0221	0.003818
0.20	0.01865	0.0221	0.003818
0.40	0.01865	0.0222	0.003822

(iii) *Determination of copper in presence of other ions.* It is clear from the results in Table IV that copper could be determined in presence of Cd^{+2}, Zn^{+2}, Pb^{+2} and Co^{+2} between pH 1.8 and 2.4 with resorcylaldoxime.

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TABLE IV

'Cu' taken in g	Metal ions added in g	Wt of 'Cu' ppt. in g	'Cu' found in g
0.019135	(Cd^{+2}) .00792	0.1103	0.01907
0.019135	.01056	0.1104	0.01907
0.019135	.03960	0.1096	0.01894
0.01248	(Zn^{+2}) .00350	0.0721	0.01247
0.01248	.01750	0.0718	0.01241
0.01248	.07020	0.0715	0.01236
0.015308	(Ni^{+2}) .00299	0.0881	0.01524
0.015308	.00598	0.0876	0.01515
0.015308	.02990	0.0860	0.01487
0.015308	(Pb^{+2}) .00445	0.0886	0.01531
0.015308	.02172	0.0885	0.01530
0.015308	.08720	0.0882	0.01523
0.019135	(Co^{+2}) .01282	0.1106	0.01912
0.019135	.02564	0.1102	0.01905
0.019135	.12820	0.1094	0.01891

(iv) *Analysis of copper in brass.* Copper in brass has been estimated by this method, with as satisfactory results as with salicylaldoxime. Two different varieties of the alloy

the alloy in the

l 2.65: (Table V).

ıd made up to 100

nl with water.

u' found in g
0.00287
0.01138
0.0316
0.0945

ution, in a 250 ml
ras then added and
re was kept on the
lass gooch crucible,
for nickel is 0.1618.

		'Ni' found in g
0.00149	0.0092	0.00148
0.00598	0.0366	0.00592
0.01495	0.0922	0.01491
0.01943	0.1203	0.01945
0.02980	0.1849	0.02990

References p. 339.

ERRATA

Anal. Chim. Acta, 12 (1955) 337, line 5 from bottom, for $4r_2^2df_2$ read $4\pi r_2^2df_2$; line 1 from bottom, for $4r_1^2df_1$ read $4\pi r_1^2df_1$.

p. 340, line 7, for $\frac{4r_1^2df_1}{4r_2^2df_2}$ read $\frac{4\pi r_1^2df_1}{4\pi r_2^2df_2}$

(ii) *Effect of the reagent concentration.* As in the case of copper it was found that at least 6-7 times the theoretical quantity of reagent was required for complete precipitation of nickel. Results are shown in Table VII.

TABLE VII

(Ni^{+2} taken 0.01495 g; 1% reagent solution)

Amount of reagent in ml	*pH of the solution*	*Wt of 'Ni' ppt. in g*	*'Ni' found in g*
5	5.5	0.0914	0.01478
10	5.5	0.0918	0.01485
15	5.5	0.0922	0.01493
20	5.5	0.0926	0.01498
30	5.5	0.0928	0.01502

(iii) *Determination of nickel in presence of other ions*

TABLE VIII

Wt of Ni taken in g	*Metal ions added in g*	*Wt of Ni ppt. in g*	*Ni found in g*
0.01495	(Cd^{+2}) 0.00792	0.0920	0.01488
0.01495	0.03960	0.0928	0.01501
0.01495	0.07920	0.0932	0.01508
0.01196	(Co^{+2}) 0.01282	0.0738	0.01194
0.01196	0.05128	0.0743	0.01201
0.01196	0.06410	0.0742	0.01200
0.01794	(Zn^{+2}) 0.0035	0.1108	0.01792
0.01794	0.0525	0.1116	0.01808
0.01794	0.0702	0.1114	0.01802
0.01495	(Mn^{+2}) 0.01671	0.0931	0.01506
0.01495	0.06684	0.0932	0.01507
0.01495	0.10030	0.0938	0.01517
0.01196	(Pb^{+2}) 0.00445	0.0744	0.01203
0.01196	0.02670	0.0745	0.01201
0.01196	0.08720	0.0748	0.01210

It is clear from the above results (Table VIII) that nickel can be determined in presence of Cd^{+2}, Co^{+2}, Zn^{+2}, Mn^{+2} and Pb^{+2} with resorcylaldoxime.

SUMMARY

Resorcylaldoxime has been used successfully for the determination of copper and nickel in presence of several metallic ions by controlling the pH. Copper-resorcylaldoxime is quantitatively precipitated from acid solution (pH 1.4). With nickel, precipitation begins at pH 4.2 and is complete between 5.54 and 6.55.

RÉSUMÉ

La résorcylaldoxime est proposée pour le dosage du cuivre et du nickel, en présence de plusieurs ions métalliques, à pH contrôlés. Le composé cuivre-résorcylaldoxime précipite quantitativement en solution acide (pH 1.4). Avec le nickel, la précipitation commence au pH 4.2 et est complète entre les pH 5.54-6.55.

ZUSAMMENFASSUNG

Das Resorcylaldoxim wird für die Bestimmung von Kupfer und Nickel vorgeschlagen, in Gegenwart von verschiedenen Metallionen bei verschiedenen pH-Werten. Die Kupfer-Resorcylaldoxim-Verbindung fällt in saurer Lösung (pH 1.4) quantitativ aus. Mit dem Nickel beginnt die Ausfällung bei pH 4.2 und ist beendet zwischen pH 5.54-6.55.

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A NEW METHOD FOR THE DETERMINATION OF OXYGEN IN ORGANIC COMPOUNDS

by

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An examination of thermodynamic data reveals that no organic compound that contains oxygen is thermodynamically stable at any temperature. At temperatures between 0° C and 1000° C and at one atmosphere pressure, every compound containing carbon, hydrogen, and oxygen would, if allowed sufficient time, decompose, yielding a more stable species of oxygen; namely, water, carbon dioxide, or carbon monoxide. The remaining carbon of the original compound would appear as methane or as elementary carbon, and the hydrogen would appear as methane or as hydrogen gas. It hardly need be added that decomposition of most organic compounds into these ultimate products proceeds with appreciable rates only at high temperatures.

The three compounds, water (in the gaseous state), carbon dioxide, and carbon monoxide, are of strikingly similar thermodynamic stability with respect to oxygen if carbon (graphite) and hydrogen (at one atmosphere pressure) are present. In Fig. 1 the logarithms of the equilibrium constants for the formation of the three compounds are plotted against the reciprocal of the absolute temperature. From the figure it is evident that at temperatures below 600° C and under standard conditions, water is, by a small margin, the most stable of the three compounds. Above 600° C carbon monoxide is the most stable. (The fact that the equilibrium constants of the three reactions of Fig. 1 are nearly the same at 630° C is presumably accidental and without particular significance.)

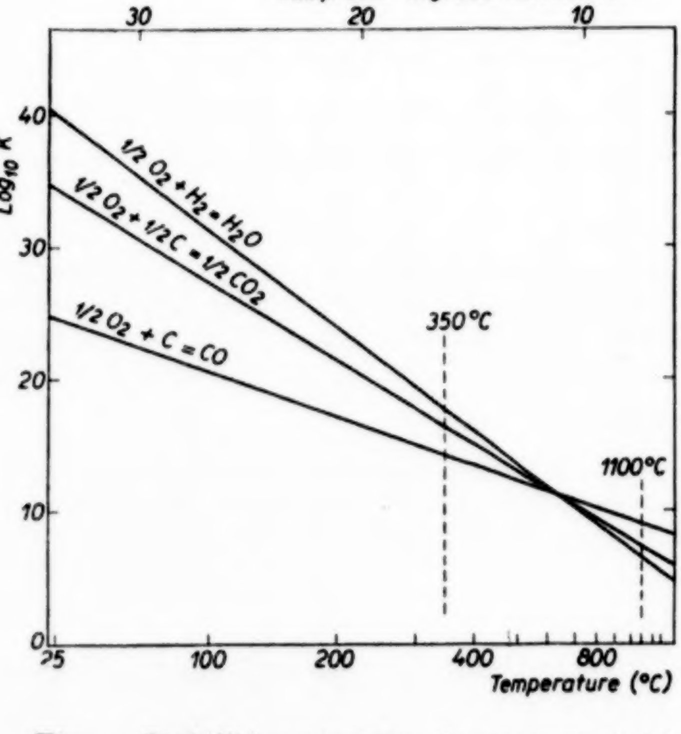

Fig. 1. Stabilities of water (in gaseous state), carbon dioxide, and carbon monoxide.

The methods[3] most frequently used for the determination of oxygen in organic compounds depend upon the conversion of the oxygen either to water, as in the TER MEULEN method[13], or to carbon monoxide, as in the Schütze-Unterzaucher method[1,2,6,7,10,16,17]. In the former method the vapor or pyrolysis products of the organic compound are passed with hydrogen over a suitable catalyst at about 350° C and the amount of water formed is determined. In the Schütze-Unterzaucher method the vapor or pyrolysis products are passed over carbon at about 1100° C and the amount of carbon monoxide is determined. The Schütze-Unterzaucher method is the more popular and reliable method[2,12]. One of the difficulties of both methods is the maintenance of conditions such that the desired compound of oxygen is obtained exclusive of the others. This difficulty is due partly to the similarity in stabilities of water and the oxides of carbon and partly to the possibility that complete equilibrium may not be attained during the relatively rapid passage of the gases through the reaction tube. In addition to the ter Meulen and the Schütze-Unterzaucher methods, a method based on the isotopic dilution principle has been described[5].

For the method described below a reagent was sought that would react, in a closed container at elevated temperature, with water, carbon dioxide, and carbon monoxide, yielding a more stable compound of oxygen. The reagent would therefore presumably also react with any compound of carbon, hydrogen, and oxygen. Among possible reagents are metal oxides, metals, and metal halides. Procedures in which *metals* and *metal halides* were used as reagents are described in the section below entitled Other Methods. *Metal oxides* may be regarded as capable of stabilizing either carbon dioxide by formation of metal carbonate, or water by formation of metal hydroxide. The determination, by common volumetric or instrumental methods, of carbonate in the presence of an excess of metal oxide is more convenient than the determination of hydroxide in the presence of excess oxide. For this reason a metal oxide was sought that would stabilize carbon dioxide to a greater extent than it would stabilize water.

The reagent was selected on the basis of information given in Fig. 2. Six bars are shown for each element, the height of each bar representing the logarithm of an equilibrium constant. The first pair of bars for each element refers to a reaction analogous to reaction (1), the second pair to a reaction analogous to (2), and the third pair to a reaction analogous to (3).

$$H_2O_g + 1/2\ SrO + C = 1/2\ SrCO_3 + 1/2\ CH_{4g} \qquad (1)$$

$$H_2O_g + SrO = Sr(OH)_{2s} \qquad (2)$$

$$1/3\ SrCO_3 + 2/3\ Sr = SrO + 1/3\ C \qquad (3)$$

The first bar of each pair refers to a reaction temperature of 25° C, the second bar to a temperature of 625° C. Only for strontium and barium are the first pair of bars positive and higher than the second pair. Consequently, only the oxides of strontium and barium would be suitable reagents. A survey of most of the metals of the periodic chart indicated the same conclusion. The comparison of equilibrium constants indicates that strontium oxide is slightly preferable to barium oxide. In addition, the preparation of pure strontium oxide is easier. Strontium oxide was therefore chosen as the reagent. However, preliminary experiments with barium oxide indicated that this compound can also be used as the reagent.

(The data necessary for thermodynamic calculations were taken from tables of the National Bank Bureau of Standards[15]. Entropies, if not given by NBS, were calculated by Latimer's method[11]. The coefficients in equations of the type (1) and (2) were chosen so as to involve 1 mole of water regardless of the valence of the metal.)

The reverse of reaction (3) represents a possible interfering reaction, the reduction of the reagent by carbon. Therefore, elements represented in Fig. 2 are also eliminated from consideration if the third pair of bars extends below the zero line (*e.g.*, potassium, silver, *etc.*).

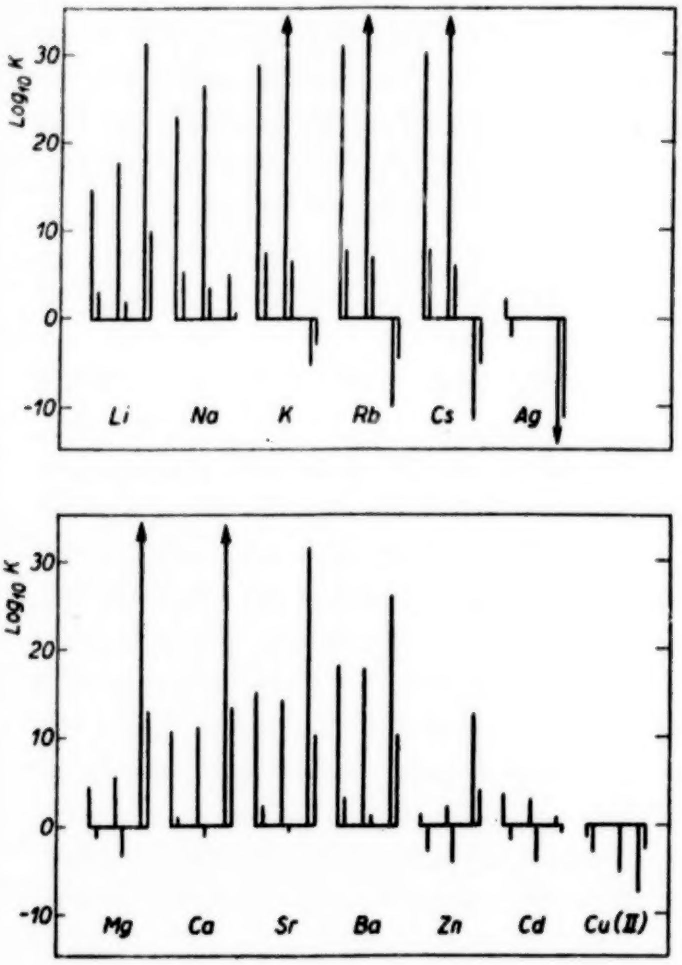

Fig. 2

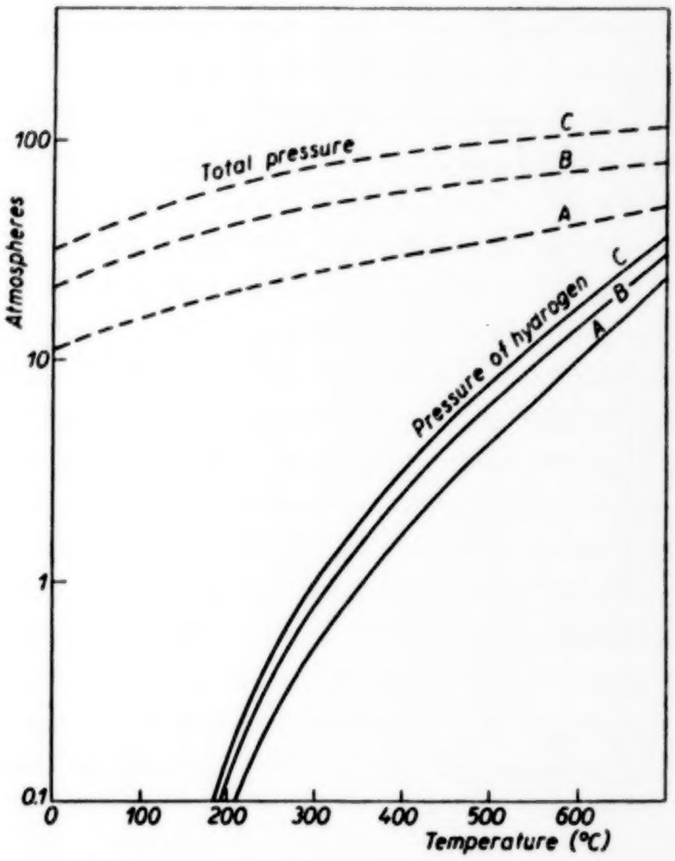

Fig. 3

Fig. 2. Stabilities of carbonates and hydroxides. (The first, second and third pairs of bars for each element give the equilibrium constants of reactions of the type (1), (2), and (3), respectively. The first bar of each pair refers to a reaction temperature of 25° C and the second bar, to a temperature of 625° C. At both temperatures crystalline solids are adopted as the standard states of the oxides, carbonates, hydroxides, and metals.)

Fig. 3. Calculated equilibrium pressures in typical analysis (nominal concentrations of hydrogen, defined as (moles H_2 + 2. moles CH_4)/(volume), is 1,2, and 3 millimoles per ml in curves A, B, and C, respectively).

The fate of the hydrogen of the sample is of interest because high pressures of hydrogen gas in the reaction vessel tend to stabilize strontium hydroxide relative to strontium carbonate. The reaction of carbon with hydrogen, yielding methane, may tend to reduce the pressure of hydrogen. The equilibrium pressures of acetylene, benzene, and other hydrocarbons, except methane, would be negligible in the temperature range 25° C to 700° C. Fig. 3 shows the calculated pressure of hydrogen that would exist in typical analyses provided that equilibrium between carbon, hydrogen, and methane

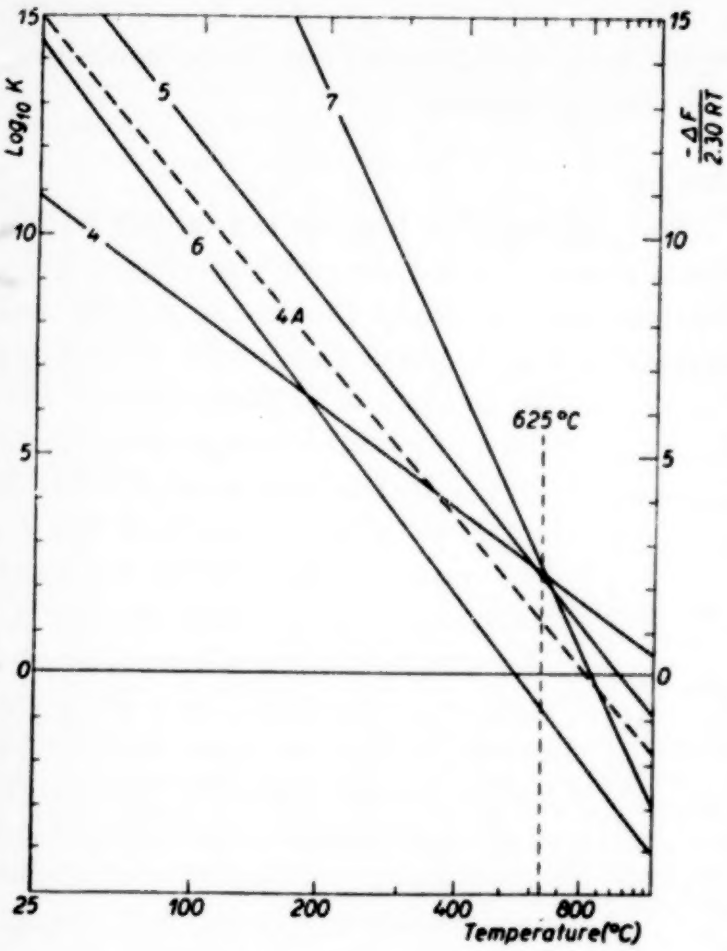

Fig. 4. Calculated equilibrium constants of reactions occurring in strontium oxide bomb. (Lines 4-7 give the logarithms of the equilibrium constants of reactions (4) — (7), respectively, all substances being in their standard states. Line 4A gives the value of $-\Delta F/2.30\,RT$ for reaction (4), assuming that the pressure of hydrogen is that calculated for a typical analysis — see Fig. 3.)

were maintained. How rapidly the hydrogen-methane equilibrium is established in the presence of strontium oxide is not known. The approach toward equilibrium may be so slow, even at 625°, that equilibrium calculations have no relation to the actual pressures.

The variations with temperature of equilibrium constants of reactions involved in the determination of oxygen are given in Fig. 4. Line 4 represents the logarithm of the equilibrium constant of reaction (4),

$$H_2O_g + 1/2\,SrO + 1/2\,C = 1/2\,SrCO_3 + H_{2g} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

Line 4A represents the comparable quantity $-\Delta F/2.30\,RT$ for a reaction similar to 4 except that the hydrogen pressure is that calculated for a typical analysis (Fig. 3) instead of one atmosphere. The position of line 4A indicates that at temperatures below 625° C water reacts quantitatively to form strontium carbonate.

Line 5 represents the reverse of the dissociation of strontium carbonate.

$$1/2\,CO_{2g} + 1/2\,SrO = 1/2\,SrCO_3 \qquad (5)$$

The dissociation is not appreciable below 1100° C.

The relative stabilities of strontium carbonate and strontium hydroxide can be found by comparison of lines 4A and 6, the latter representing the reaction

$$H_2O_g + SrO = Sr(OH)_{2s} \qquad (6)$$

Although lines 4A and 6 are not far apart the difference between them is especially significant at 625° C. At this temperature strontium hydroxide is completely dissociated into water and strontium oxide. The water vapor is then available for a relatively rapid reaction with carbon and strontium oxide, the product being strontium carbonate.

Line 7, representing the reaction,

$$CO_g + 1/2\,SrO = 1/2\,SrCO_3 + 1/2\,C \qquad (7)$$

is of interest in the preparation of strontium oxide reagent. It can be seen from the figure that strontium carbonate reacts with carbon at a temperature about 200° lower than dissociation temperature. In practice the most convenient method[18] of preparation of strontium oxide is the heating of an intimate mixture of graphite and strontium carbonate to 1100° C. It was found possible to prepare strontium oxide containing less than 0.1 mole per cent carbonate by this procedure.

RESULTS

The procedure, described in full detail below, consisted in heating the sample with a mixture of strontium oxide and graphite in a sealed Vycor tube or nickel bomb. After heating, the strontium carbonate was decomposed by acid and the carbon dioxide was collected in alkali and determined volumetrically. Fig. 5 shows the results of analyses for oxygen in hydroquinone. The correct amount of oxygen was found after a heating period of 2 hours at 650° C or after 14 hours at 550° C. The recommended period for most compounds is 3 hours at 650° C. The results of the analyses of several organic compounds are given in Table I. The error in analyses of hydroquinone, tartaric acid, benzoic acid, and dextrose was 0.3% or less (absolute error). Analyses of phenol and xanthone gave low results (Table I). These compounds were chosen because they are very resistant to complete pyrolysis to oxides of carbon or to water even if heated to 900° C for several hours[8]. Analyses of phenol, diphenyl ether, and xanthone by the SCHÜTZE-UNTERZAUCHER method have apparently not been reported in the chemical literature.

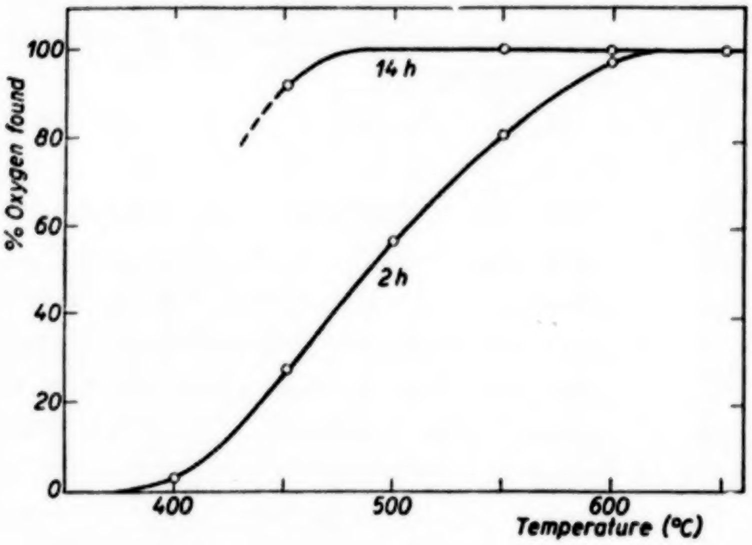

Fig. 5. Determination of oxygen in hydroquinone (Reactions carried out in sealed Vycor tubes).

The strontium oxide method appears to be applicable to samples containing carbon, hydrogen, and oxygen only. Compounds containing nitrogen gave high results. Urea was found to contain 33.9% oxygen (theoretical, 26.6%) and picric acid was found to contain 56.2% (theoretical, 48.9%). These high results may be due to the formation of some strontium cyanide and the consequent liberation of oxygen from strontium oxide. This explanation is not consistent, however, with thermodynamic calculations in which a state of chemical equilibrium is assumed. Sulfur and halides would be expected from thermodynamic considerations to yield high results because of the formation of barium sulfide and barium halides. (However, it may be possible to determine the sum of oxygen and halogen by the method).

A modification of the strontium oxide method was used to determine *carbon* in hydroquinone. The sample was heated in a nickel bomb with pure barium nitrate, and the barium carbonate which formed was determined. In this procedure the barium nitrate served as a source of both barium oxide and oxygen, and the carbon in the sample was converted to barium carbonate. (Interference by nitrite in the determination of carbonate was minimized or eliminated by addition of chromate to the distilling flask A of Fig. 7). The amount of carbon found in hydroquinone was 65.2% (theoretical, 65.45%). The method was not tested with other organic compounds.

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TABLE I

RESULTS OF ANALYSES FOR OXYGEN

Compound	*Container*	*Conditions*	*Percentage Oxygen* *Theoretical*	*Percentage Oxygen* *Found*
Hydroquinone	Vycor tube	650° C, 3 h	29.06	29.4
Tartaric acid	Nickel bomb	,, ,,	63.96	63.8
Benzoic acid	,, ,,	,, ,,	26.20	26.5
Dextrose	,, ,,	,, ,,	53.29	53.2
Phenol	,, ,,	,, ,,	17.0	14.4
	,, ,,	700° C ,,	17.0	15.6
Xanthone	,, ,,	650° C ,,	16.3	8.6
	,, ,,	700° C ,,	16.3	10.1

EXPERIMENTAL DETAILS

Procedure. A sample containing 0.5 to 2 millimoles of oxygen is weighed in the nickel bomb shown in Fig. 6. For a compound containing 30% oxygen the quantity of the sample would be about 30-110 mg, the latter weight being preferred. (Volatile liquid samples can be weighed in thin-walled capillary tubing fabricated from Vycor. Liquid samples have not yet been analyzed by the strontium oxide method.) About 0.8 of graphite-strontium oxide mixture, equivalent to about 6 millimoles of strontium oxide, is added rapidly and with minimum exposure to the moisture and carbon dioxide of the atmosphere. A convenient tool for the rapid addition of a reproducible amount of reagent is a glass cup mounted on the end of a glass handle. After the addition of reagent the bomb is immediately covered.

A "blank" is prepared at about the same time by adding the same amount of reagent, but no sample, to a nickel bomb. The bomb containing the sample and that containing no sample are

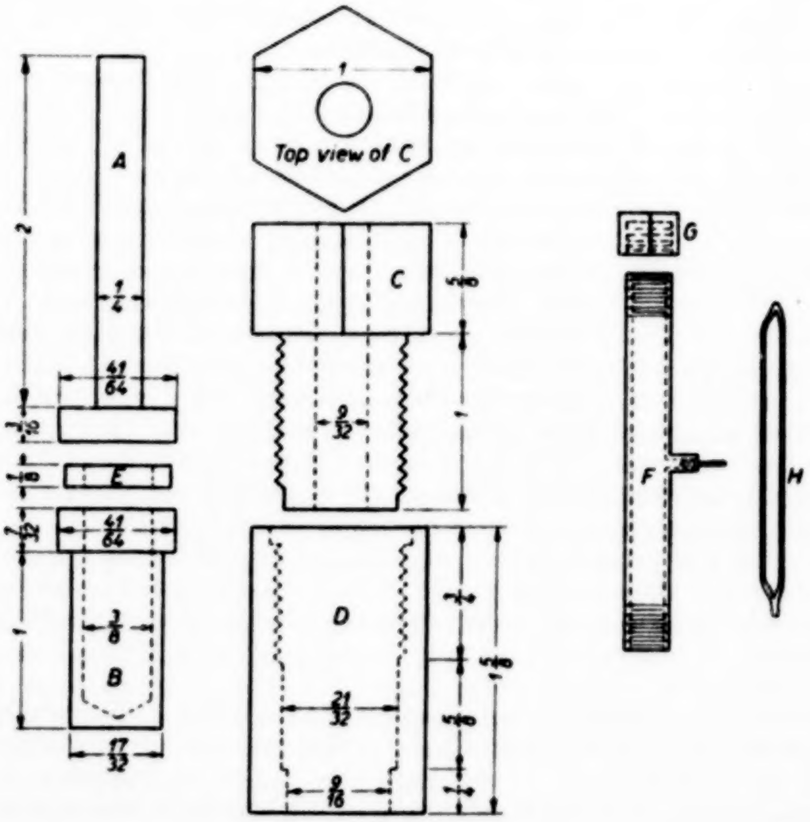

Fig. 6. Bomb assembly (Parts A-E), apparatus for breaking Vycor reaction tubes (Parts F-G), and sealed Vycor tube (H) (All dimensions are in inches.)

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treated, as nearly as possible, identically in all subsequent steps of the procedure. The blank serves to cancel out or minimize errors due to carbonate and hydroxide impurities in the reagent, atmospheric oxygen initially in the bomb, and absorption of atmospheric carbon dioxide during the determination of carbonate. The blank also eliminates the necessity of using standardized sodium hydroxide in the procedure described below.

Graphite is applied to the threads of the yoke, and the yoke is put on the bomb and tightened in a vice with a wrench 12 inches long. The bomb assembly is put into an electric oven maintained at 650° C and is allowed to remain 3 hours. The bomb assembly is then cooled in an air blast and the yoke is removed. If the top of the bomb does not loosen during unscrewing the yoke, the base of the bomb is put into the chuck of a lathe, and the top is slowly pulled away by means of the tail stock chuck. This procedure serves to release the methane and hydrogen, present at relatively high pressure, without loss of an appreciable amount of the powder that is in the bomb. The bomb is subsequently kept covered at all times to prevent absorption of atmospheric carbon dioxide. The bottom part of the bomb is then placed in the distilling flask of the apparatus shown in Fig. 7.

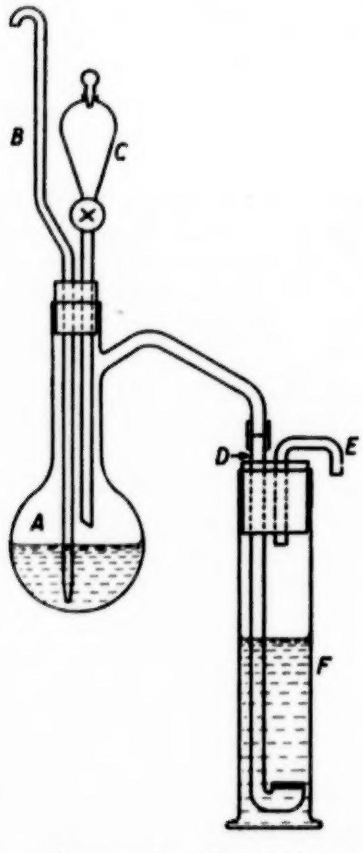

Fig. 7. Apparatus for determination of carbonate.

If a Vycor glass tube is used in place of the nickel bomb, the procedure is the following: One end of a Vycor tube of 7 mm outside diameter is sealed in a gas-oxygen burner. The temperature of the flame is then slowly reduced so that the Vycor is to some extent annealed. The empty tube is weighed, a sample containing 0.5 to 2 millimoles of oxygen is introduced, and the tube is weighed again. Approximately 0.8 g of the graphite-strontium oxide reagent is put in the tube by means of a funnel and the glass cup mentioned above. The open end of the tube is then sealed and annealed. The end of the tube that contains the sample should, during this procedure, be protected from heat by wet, cold blotting paper rolled into a cylinder. The tube, after being put into a cylinder of wire screen for protection in event of explosion, is heated for 3 hours at 650° C. After being cooled the Vycor tube is put into the stainless steel cylinder shown in Fig. 6. The end caps are screwed on and the pin is hit with a hammer. Usually the pressure of methane and hydrogen cause the Vycor tube to shatter into tiny fragments. The contents of the stainless steel cylinder are poured into flask A of the apparatus shown in Fig. 7. The cylinder is rinsed with water and the rinsings are collected in the flask.

The procedure for determination of the carbonate in the mixture is the following:

Glass cylinder F of Fig. 7 is flushed with nitrogen to remove atmospheric carbon dioxide. Twenty-five ml of carbonate-free solution, approximately $0.1N$, is added from a pipet. Approximately 10 ml of $1M$ $BaCl_2$ and 25 ml of boiled, distilled water are added. The cylinder is then stoppered with an ordinary stopper to prevent absorption of atmospheric carbon dioxide.

The distilling flask A, which is initially dry, is flushed with nitrogen. The nickel bomb and contents (or the broken Vycor tube and contents) are added. Twenty ml of boiled, distilled water are added, and the top is put in place. The Ascarite tube is connected to tube B. Tube D is filled to the top with water and inserted in cylinder F. The purpose of filling D with water is to prevent the barium solution from entering the fritted glass and from subsequently reacting with carbonate to form barium carbonate which would clog the pores. Tube D is quickly joined to the arm of the distilling flask. The needle valve, connected by rubber tubing between the aspirator and tube E, is adjusted so that air is drawn through the apparatus at the rate of about 20 ml per minute.

Approximately 30 ml of $1M$ perchloric acid is added to the distilling flask A from the separatory funnel. The distilling flask is then heated gently with a Tirrill burner. The burner is held by hand so that it can be removed rapidly if the solution enters the air inlet tube B. The solution is boiled for about 10 minutes.

Tube D is disconnected from the distilling flask, and the rubber tube from the aspirator is immediately disconnected from the cylinder at E. The cylinder and contents are cooled to room temperature. The solution in the cylinder and in the dispersion tube D is quantitatively transferred to a 250 ml conical flask that has been flushed with nitrogen. The flask is covered and a stream of nitrogen is passed over the solution to prevent the absorption of atmospheric carbon dioxide. One-tenth ml of 0.1% thymolphthalein is added and the mixture is titrated to a pale blue color with standard $0.1N$ hydrochloric acid solution.

Calculation of results. The pH at the end-point, approximately 10, is such that essentially all of the excess hydroxide ion is converted to water and none of the carbonate, present as insoluble barium carbonate, reacts. The amount of oxygen in the sample is calculated from the equation

$$\text{Millimoles of oxygen} = N_a\ (V_{\text{blank}} - V_{\text{sample}})$$

where N_a designates the normality of the acid and V designates the volume of acid used in the titration.

A typical blank corresponded to approximately 0.06 millimole of oxygen, of which about 0.02 millimole was found to be due to carbonate and hydroxide impurities in the strontium oxide-graphite reagent, 0.03 millimole (calculated) was due to atmospheric oxygen in the bomb before heating, and 0.01 millimole was found to be due to atmospheric carbon dioxide absorbed during the determination of carbonate. The amount of atmospheric oxygen in the bomb before heating is undoubtedly very reproducible.

Nickel bomb. The bomb, shown in Fig. 6, is similar to that described by KIMBALL AND TUFTS[9] but is smaller, can be heated to 700° C, and differs in details of design. (The threaded parts of the KIMBALL AND TUFTS bomb tend to stick together if heated above 550° C[14]. Parr Combustion Bombs cannot be heated in a furnace much above 400° C because of the brass yoke). Since the bomb of Fig. 6 has a volume of only 2 ml, it is not necessary to remove atmospheric oxygen before sealing it. The cup of the bomb is small enough to pass through the neck of the distilling flask. The bomb and contents can therefore be placed inside the flask.

Parts A, C, and D are machined from 18-8 stainless steel. Part B, the cup, is nickel, and part E, the gasket, is copper. The top of part B is provided with a circular recess 0.005 inch deep to accommodate and center the copper gasket. A similar recess in part A is not desirable because it would render opening of the bomb more difficult. The threads of parts C and D are cut with 3/4 inch tap and die. Before being used for the first time parts C and D are heated to 700° C for three hours to provide oxidized surfaces[9]. *Each time the bomb is assembled, a thick paste of graphite and oil is applied liberally with a brush to the threads of the yoke.* This is necessary to prevent parts C and D from being welded together during heating. Copper and nickel are to some degree welded together under the conditions of the procedure for determination of oxygen, and after the first heating the gasket becomes an integral part of the base of the bomb B. The copper does not become welded to the stainless steel top, part A. The coefficients of expansion of the materials are such that pressure on the gasket, and hence the effectiveness of the seal, increases with temperature[9]. With use the copper gasket becomes sligthtly thinner and slightly wider. When the diameter of the gasket approaches the diameter of the top of part B, the gasket should be turned down in a lathe, or removed from B and replaced. Otherwise, part B eventually becomes jammed tight in part D.

Vycor tubes. A very hot flame is required for sealing the Vycor tube. The length of the tube after being sealed at both ends, should be about 5 1/2 inches. Pyrex cannot be used in place of Vycor. Analyses of hydroquinone, in a series of experiments similar to those of Fig. 1 except that Pyrex tubes were used, gave low and erratic results. It was concluded that some barium carbonate was fused to the surface of the Pyrex and was not recovered subsequently.

The device for breaking Vycor reaction tubes is shown in Fig. 6. The stainless steel tube (F) is 6 inches long and the inside diameter is 3/8 inch. A cap (G) is provided for each end.

Apparatus for determination of carbonate. The apparatus is in several respects similar to that of FARRINGTON, NIEMANN, AND SWIFT[4] and to that of HINKEL AND RAYMOND[7]. Carbon dioxide, liberated from strontium carbonate by acid, is carried from the 125 ml distilling flask A of Fig. 7 to the cylinder F by a stream of air. Tube E is connected to a trap and aspirator. The rate of flow of air is controlled by a brass needle valve between E and the trap. The inlet tube B is connected by rubber tubing to a long drying tube filled with Ascarite, which absorbs carbon dioxide from the incoming air. The diameter of the opening of tube B at the lower end is 2 mm. A smaller opening would be clogged by carbon. The gas dispersion plate at the end of the tube D is Corning extra coarse fritted glass. Cylinder F is a 100 ml cylinder that has no pouring lip. Tube D is joined to the side arm of the distilling flask with a short length of Tygon tubing.

The method for the determination of carbonate was tested with pure sodium carbonate. The correct results were obtained with an average deviation of ± 0.2%. The "blank", found by an experiment in which no carbonate was added to the distilling flask, corresponded to about 0.1 ml of 0.1N HCl.

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Preparation of strontium oxide-graphite reagent. Twelve g of AR grade strontium carbonate is added to 6 g of pure graphite, and the mixture is ground in a mortar to a fine powder that appears uniform to the eye. (The graphite used in the experiments of Table I was grade SP-2, spectrographically pure, obtained from National Carbon Company.) Over the mixture, in a nickel crucible, is placed a layer of 1.5 g of graphite. The crucible is covered with a nickel cover and then heated in an electric oven to 1100° C for about 12 hours. The mixture, after being cooled, is rapidly ground to a powder in a mortar under a stream of nitrogen. The reagent is protected as thoroughly as possible from atmospheric moisture and carbon dioxide, and is stored in a screw cap bottle in a desiccator containing barium oxide.

The reagent might be prepared more conveniently if AR grade strontium oxide, which contains only a few mole per cent carbonate and hydroxide, is used instead of strontium carbonate in the procedure described above.

The amount of carbonate in the reagent should be less than about 0.03 milli-equivalents per gram. The carbonate content of the reagent can be found by the procedure described above, beginning with the addition of 1 g of reagent to the distilling flask. A "blank" determination, in which the reagent is not added to the flask, should also be carried out.

Barium oxide was prepared by heating AR grade barium nitrate in a platinum dish in an electric furnace under an atmosphere of nitrogen. Decomposition of the nitrate occurred without violence at 725° C and appeared to be complete after one hour. The temperature was then increased to 1000° C. Attempts to purify AR grade BaO by heating were not successful because of the high temperature (about 140° C) required for the decomposition of barium carbonate.

Organic compounds. Analytical reagent grade tartaric acid, benzoic acid, dextrose, phenol, and urea were crushed to fine powders in an agate mortar and dried at room temperature for one week in a desiccator containing magnesium perchlorate. The xanthone and picric acid were recrystallized twice from ethanol and dried as described above.

OTHER METHODS

Experiments indicated that two other methods, based on the reactions of oxygen with a metal and with a metal halide (see introduction), might be used for the determination of oxygen. In one method the sample of hydroquinone was heated to 600° C for 3 hours in a Vycor tube with zinc and a small amount of mercury. The product was then added under an atmosphere of nitrogen to an ammonia-ammonium chloride solution, and the mixture was boiled in order to dissolve zinc oxide. (The amount of amalgamated zinc that dissolved under these conditions was negligible.) The concentration of zinc in the solution was determined polarographically. Ninety per cent of the oxygen in hydroquinone was found. Magnesium, aluminium, and other metals would also be expected to convert water to the metal oxide. For these metals the determination of the oxide in the presence of an excess of the metal appears to be more difficult than for zinc.

In the second method the sample was heated in a Vycor tube with aluminum iodide. The oxygen of the organic compound was expected to cause the formation of an equivalent amount of aluminum oxide and of iodine. The iodine was titrated with thiosulfate solution. A single analysis of hydroquinone gave 85% of the theoretical amount of oxygen. The iodine-hydrogen iodide equilibrium is a possible source of error, but in principle this error can be made negligible if the hydrogen-methane equilibrium can be established. Magnesium iodide may be superior to aluminum iodide as the reagent because the former is relatively stable in air.

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SUMMARY

Oxygen in compounds of carbon, hydrogen, and oxygen can be determined by heating the sample with an excess of strontium oxide and graphite in a nickel bomb or sealed Vycor glass tube. During the heating period, three hours at 650° C, the oxygen of the sample is converted to carbonate. The carbonate is then determined volumetrically. The accuracy of the method was found to be ± 0.3% (absolute percentage error) for several types of compounds. Most elements other than carbon, hydrogen, and oxygen interfere. Compounds like phenol, that are exceedingly resistant to complete pyrolysis, yield low results. Carbon in organic compounds can be determined by heating the sample with barium nitrate, and subsequently determining carbonate in the mixture.

RÉSUMÉ

L'oxygène dans les composés organiques, formés de carbone, d'hydrogène et d'oxygène, peut être dosé par chauffage de l'échantillon à analyser, en présence d'un excès d'oxyde de strontium et de graphite dans une bombe de nickel ou dans un tube de verre scellé de Vycor. Pendant le chauffage, 3 heures à 650° C, l'oxygène est converti en carbonate. Le carbonate formé est ensuite dosé volumétriquement. La précision de cette méthode est de ± 0.3% (pourcentage d'erreur absolue) pour plusieurs types de composés. La plupart des éléments, autres que le carbone, l'hydrogène et l'oxygène, gêne. Des composés tels que le phénol, excessivement résistants à la pyrolyse, donnent des résultats trop faibles. Le carbone dans les composés organiques peut être dosé par chauffage avec le nitrate de baryum et ensuite par détermination du carbonate formé.

ZUSAMMENFASSUNG

Der Sauerstoff in organischen Verbindungen, welche aus Kohlenstoff, Wasserstoff und Sauerstoff bestehen, kann bestimmt werden durch Erhitzen der zu analysierenden Substanz in einer Nickelbombe oder in einem zugeschmolzenen Glas von Vycor in Gegenwart eines Überschusses von Strontiumoxyd und Graphit. Während der dreistündigen Erhitzung bei 650° C wird der Sauerstoff in Karbonat umgewandelt. Das gebildete Karbonat wird darauf volumetrisch bestimmt. Die Präzision dieser Methode ist für verschiedene Arten von Verbindungen ± 0.3% (Prozent des absoluten Fehlers). Die meisten andern Elemente, als der Kohlenstoff, der Wasserstoff und der Sauerstoff, stören. Verbindungen wie Phenol, äusserst widerstandsfähig gegenüber der Pyrolyse, geben zu schwache Resultate. Der Kohlenstoff in organischen Verbindungen kann bestimmt werden durch ein Erhitzen mit Bariumnitrat und darauf durch eine Bestimmung des gebildeten Karbonates.

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PAPER CHROMATOGRAPHY OF INORGANIC IONS
XI. THE BEHAVIOUR OF SOME COBALT (III) COMPLEXES

by

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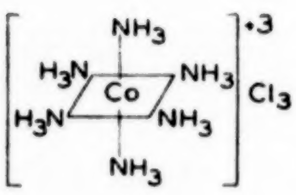
In previous papers of this series the position of ions in several solvents was mapped so as to provide data both for analysis and the extractability of ions.

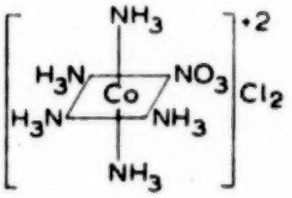
Recently we have separated ^{58}Co and ^{55}Fe from irradiated Mn and it occurred to us that during the process of concentration and preliminary separation *e.g.* precipitation of $Fe(OH)_3$ with Al carrier, the Co(II) present may easily be oxidized in presence of ammonia to yield a stable Co(III) complex. It was also considered of interest to examine Co(III) complexes carrying different charges but otherwise similar so as to observe the effect of the net charges on the R_F values.

The following cobalt complexes were prepared according to the methods described in the book of PALMER[1]:


NH3
H3N
NH3
Co
H3N
NH3
NH3
+3
Cl3

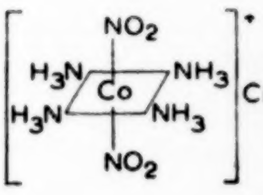
I

hexammino-cobalt (III) chloride


NH3
H3N
NO3
Co
H3N
NH3
NH3
+2
Cl2

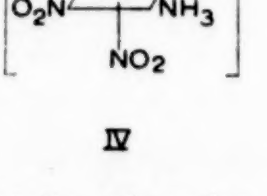
II

nitrato-pentammino cobalt(III) chloride


NO2
H3N
NH3
Co
H3N
NH3
NO2
+
Cl

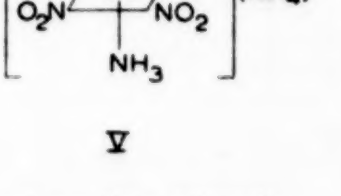
III

trans-dinitro-tetrammino cobalt(III) chloride


NH3
O2N
NH3
Co
O2N
NH3
NO2
0

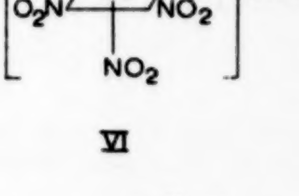
IV

trinitro-triammino cobalt(III)


NH3
O2N
NO2
Co
O2N
NO2
NH3
-
(NH4)+

V

ammonium tetranitro-diammino cobaltate(III)


NO2
O2N
NO2
Co
O2N
NO2
NO2
-3
3 Na+

VI

sodium hexanitro-cobaltate(III)

The tetrammino-dinitro-cobalt(III) chloride was not purified and contained appreciable quantities of pentammino-mononitro-cobalt(III) dichloride.

THE BEHAVIOUR OF THE COBALT COMPLEXES IN VARIOUS SOLVENTS

Acetone-HCl-water

A mixture of acetone-HCl-water (90:5:5) was first described by BURSTALL *et al.*[2] for the separation of Ni, Mn, Co, Cu, Zn and Fe, and has been used by us for numerous separations of radioelements[3,4]. It was shown that carrier-free isotopes have the same R_F values as macro-quantities, when the non-complexed ions are run on the paper.

The position of the cobalt complexes after development is shown in Fig. 1. Thus of all the complexes examined only V is sufficiently decomposed to yield a spot with the R_F value of Co(II) ion. It is important to note that the very stable cationic complexes I, II and III all stay in the region also occupied by Ni.

Butanol-HCl 1*N*

In this solvent complexes I, II and III stay almost at the point of application. The complex III yields also a spot of the same R_F value as IV, that is a spot of a neutral complex, while V is decomposed to give a spot of the R_F of Co(II) and VI is slowly decomposed leaving a comet. All spots are shown in Fig. 2.

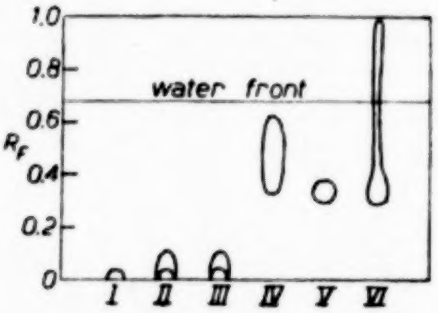


Fig. 1. Solvent: acetone 90, HCl 5, water 5.

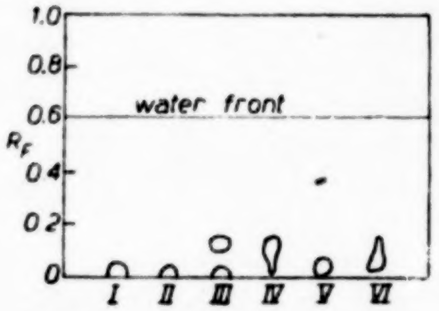


Fig. 2. Solvent: butanol saturated with 1*N* HCl.

Butanol-ammonia

In butanol shaken with 1.5*N* aqueous ammonia all six complexes were found on the point of application.

Butanol-acetic acid

This solvent is of theoretical rather than practical interest because all the six complexes are stable in dilute acetic acid. Fig. 4 shows the movement of the complexes with the mixture butanol-acetic acid-water (100:20:80). Contrary to expectation cobaltinitrite yielded numerous spots and as these change colour during development they must be considered as decomposition products. Otherwise the trend of the R_F values appears to be that the R_F value decreases with an increase of ionization.

An attempt was made to increase the R_F values by adding some ethyl alcohol to the solvent mixture. However the results in butanol-ethanol-acetic acid-water (90:10:10:90) are not essentially different from those in the previous solvent. See Fig. 3.

In all cases there is evidence for the presence of more than one ionic species with complexes II, III, IV and VI either due to decomposition during development or to the presence of impurities from the synthesis.

Water

We also examined the movement of the cobalt complexes with distilled water as solvent. Previous work with amino acids and other substances[5] indicated that the most ionised substances are most strongly adsorbed on paper owing to the ion exchange properties of ordinary filter paper. We were surprised to note that this was not the case with cobalt complexes. Complexes III and IV which are monovalent and neutral, respectively, travel much slower on paper than trivalent and divalent anions and cations as shown in Fig. 5. We can not offer any explanation for this behaviour at the moment.

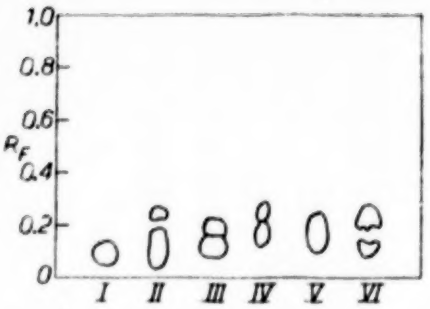


Fig. 3. Solvent: butanol 90, ethanol 10; acetic acid 10, water 90.

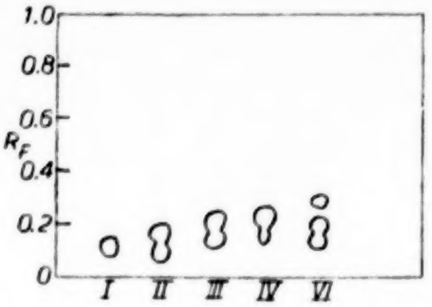


Fig. 4. Solvent: butanol 100; acetic acid 20, water 80.

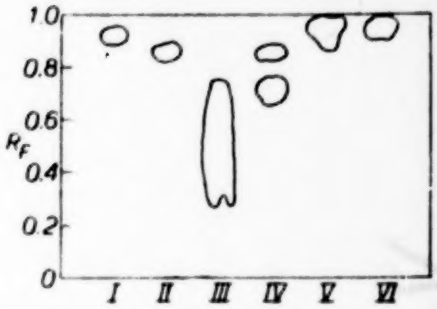


Fig. 5. Solvent: water.

SUMMARY

The R_F values of six cobalt (III) complexes in butanol/HCl, butanol/NH_3, butanol/acetic acid, acetone-HCl and water were measured. In organic solvents the least ionized complex travels fastest unless decomposed. In water the highly ionized complexes travel faster than the monovalent or neutral complexes.

RÉSUMÉ

Les valeurs de R_F de six complexes du cobalt(III) ont été mesurées dans les mélanges suivants: butanol/HCl, butanol/NH_3, butanol/acide acétique, acétone/acide chlorhydrique et eau. Dans les solvants organiques, le complexe le moins ionisé marche le plus rapidement. Dans l'eau, les complexes les plus fortement ionisés marchent plus rapidement que les complexes monovalents ou neutres.

ZUSAMMENFASSUNG

Die Werte für R_F von sechs Kobalt(III)-komplexen sind in folgenden Mischungen gemessen worden: Butanol/HCl, Butanol/NH_3, Butanol/Essigsäure, Azeton/Salzsäure und Wasser. In den organischen Lösungsmitteln wandert der am wenigsten ionisierte Komplex am schnellsten. Im Wasser wandern die am stärksten ionisierten Komplexe schneller, als die einwertigen oder neutralen Komplexe.

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CHROMATOGRAPHIC EXAMINATION OF METALLIC IONS
II. STABILITY OF ANTIMONY HALIDE COMPOUNDS

by

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INTRODUCTION

The effect of anions present in a solution of metallic ions taken from chromatographic analysis does not appear to have been examined, although some authors[1,2], by implication, seem to be aware of the possible effects.

During a recent investigation, ANDERSON AND MARTIN[3] found that certain ions *e.g.* As(III), Sb(III), Tl(III), Au(III), Hg(II), Sn(II) and Sn(IV) and some of the precious metals when applied as the chloride, maintained substantially the same R_F values, irrespective of the nature of the solvent, for about a dozen different butanol-water chelating acid mixtures. It seemed possible that the above ions were travelling as the chloride complex and were unaffected by the organic acid in the butanol solvent. Of the above, some metal ions were travelling above the "adsorption front"[3] and so were not in contact with the chelating agent.

As(III) and Sb(III) ions were in general found to travel below the adsorption front, and so would have been expected to react with the chelating agent (a) if compounds could be formed with it and (b) if the compounds so formed were more stable in this environment than the $AsCl_3$, or $SbCl_3$ taken for testing.

Antimony in its halide compounds (trivalent) and antimonyl tartrate were chosen to investigate the change of ligand during chromatographic analysis. To check the effect of acid concentration in the metal solution on the R_F value, a series of acidities was taken with antimony chloride and hydrochloric acid and a separate series of tests done on them.

EXPERIMENTAL

The antimony compounds of the halides were prepared by taking freshly precipitated antimony tri-sulphide, dissolving in pure halide acid and evaporating to dryness. The solutions were prepared by taking sufficient of these salts to make 30 ml of 0.1*M* solution of antimony and dissolving in approximately 4*M* acid. The series of antimony chloride solutions to test the effects of acidity on R_F value were made in the same way except that the acid concentrations were 10*M*, 8*M*, 7*M*, 6*M*, 5*M*, 4*M*, 3*M*, 2*M*, 1*M* and 0.5*M* saturated with KCl. The antimonyl tartrate solution was made from potassium antimonyl tartrate again 0.1*M* in neutral solution.

The solvent solutions were prepared from freshly distilled butanol by shaking equal volumes of butanol and 2*N* aqueous acid. The butanol rich phase was used after separation. About 5 ml of butanol was added to stabilize the solution against temperature drop. The acids used were of analytical reagent quality. The hydrobromic and hydriodic acids were freshly distilled and about 1% of hypophosphorous acid was added to the latter to stabilize it. The hydrofluoric acid solution was stored in a paraffined bottle.

The ascending technique was used. The containers were 3-quart Winchester bottles from which the top had been cut and the glass edge ground flat. The top was covered with a glass plate. The solvent was contained in a 9 cm Petrie dish supported on glass wool. The aqueous phase was placed in the Winchester, outside the Petrie dish and to saturate the atmosphere in the container more rapidly the sides were also wet with the aqueous phase.

Schleicher and Schull 598 paper was used in sheets approximately 29 cm by 18 cm. The metal solution was spotted on at intervals of 2.5 cm along the long side of the paper and 3 cm from the edge. The spots contained about 0.02 ml of solution. The paper was coiled into a cylinder 18 cm high and about 9 cm diameter and after air drying, placed in the solution in the Petrie dish. No equilibration was used.

The temperature remained at 20 to 23° C for the series and the humidity of the laboratory remained constant at 60 to 70% relative humidity during the course of the experiments. Each run took about two hours and the liquid rose approximately 15 cm.

The position of the antimony was found by exposing the paper to H_2S gas. In the case of the hydriodic acid a considerable amount of free iodine was liberated on the paper. Prolonged exposure to H_2S gas reduced this to iodide and left the antimony spots clearly defined.

The spots were roughly oval in shape with the shorter axis in the direction of travel. The R_F value was measured from the centre of greatest density of the spot to the original position and referred to the distance of travel of the liquid front. Consequently all values were less than unity.

The partition coefficients were determined by shaking about 0.5 g of antimony salt with 100 ml of butanol and 100 ml of $2N$ acid, after 30 min shaking the mixture was allowed to settle and 25 ml aliquots were taken from the aqueous and butanol layers. The antimony was precipitated by passing H_2S, and the Sb_2S_3 filtered and weighed as such after drying at 175° C to constant weight. The values given in Table I are for the quantity of antimony in butanol phase relative to the quantity in the same volume of aqueous phase.

RESULTS

The various concentrations of hydrochloric acid and for $0.5N$ HCl and saturated KCl gave no significant difference in R_F value; mainly lying within $R_F \pm 0.02$. The values were: 0.71, 0.72, 0.72, 0.70, 0.67, 0.70, 0.73, 0.73, 0.71.

The partition coefficients are given in Table I.

TABLE I

Compound	*Partition Coefficient*
SbI_3	20.9
$SbBr_3$	3.7
$SbCl_3$	0.50
$(SbO, C_4H_4O_6)^-$	0.06

The R_F values for the various halide ions and for the tartrates are given in Table II.

TABLE II

Acid in developing agent	*R_F value of antimony in acid solution*				
	H_2F_2	*HCl*	*HBr*	*HI*	*$C_4H_6O_6$*
H_2F_2	0.09	0.70	0.74	0.78	0.08
HCl	0.68	0.76	0.80	0.85	0.70
HBr	0.80	0.78	0.81	0.85	0.79
HI	0.72	0.72	0.73	0.75	0.73
$C_4H_6O_6$	0.20	0.71	0.74	0.83	0.10

DISCUSSION

It is generally assumed[4] that the antimony-ligand bond in antimony chloride, antimony bromide and antimony iodide is more or less covalent while in the fluoride the bonding is largely ionic. In the case of the antimony tartrate or antimonyl tartrate the position is less certain but is probably $[Sb = O]^+$, both bond types being present. This is borne out by the results of the partition coefficients in Table I. If it is assumed that the covalent bond is a more stable bond than the ionic, we have an explanation of the fact that the R_F values (see Table II) of antimony fluoride and antimony tartrate are substantially the same as the chloride, bromide or iodide when measured using butanol hydrochloric, butanol hydrobromic or butanol hydriodic solvents. When butanol hydrofluoric and butanol tartaric solvents are used, the R_F values of the antimony tartrate and antimony fluoride is low as no halide is present to form a covalent compound with the antimony ions. On the same chromatogram the other antimony halides have their usual R_F values.

It seems clear that an exchange reaction, such as:

$$2Sb^{+3}F_3^- + 6H^+ + 6Cl^- \rightarrow 2SbCl_3 + 3H_2F_2$$

which is not reversible under the conditions of the experiment, occurs.

The evidence for an exchange of ligand between say, antimony chloride and the acid of another halide, *e.g.*

$$SbCl_3 + 3H^+ + 3Br^- \rightleftarrows SbBr_3 + 3H^+ + 3Cl^-$$

is not so clear cut, but is strong enough to assume that this probably happens.

The concentration of antimony taken is of the order $1 \cdot 10^{-6}$ mol and occupies 1 sq.cm of paper. The acid concentration on the paper is of the order of $3 \cdot 10^{-4}$ mol[5] an excess which would normally ensure that the reaction moved to the right. However, in the reverse case, $SbBr_3$ spot and HCl solvent, the reverse should take place and a spot with an R_F value, the same as for the $SbCl_3$, should be obtained. This does not happen and individual and separate spots for the chloride and bromide are obtained.

It seems that the antimony chloride, bromide and iodide have successively greater stabilities, greater than can be decomposed with a 300 fold greater concentration of lower molecular weight halide acid.

A clear separation on the basis of solubility in the organic phase would be possible if the ratio of the solubility products of the two halides differed by a large amount. However, reference to Table I shows only a six fold difference. Under these conditions considerable trailing could be expected if the separation depended on solubility alone. The clear spots obtained suggest that solubility plays only a small part in the separation, compared with bond strength.

The R_F values obtained using hydriodic acid-butanol solvent are in general rather lower than for other acids. This is probably due to the decomposition of the hydriodic acid by the paper with the liberation of iodine. This will give a lower adsorption front and hence lower R_F values.

The formula of Martin and Synge[6] relating R_F value and partition coefficient a

$$R_F = \frac{A_L}{A_L + aA_S}$$

References p. 356.

is accepted as correct for amino acid separations. A difficulty arises when work is done with solvents which separate into zones on the paper. Here the ratio A_L/A_S is no longer, even approximately[6], constant over the paper and a direct application of the formula is impossible until more precise information on this matter is available. There is a general agreement between the data of Tables I and II in that increasing partition coefficients correspond with increasing R_F values.

CONCLUSION

It is clear from the above data that the R_F value of a metal ion is dependent on the anion in the original solution where there is a possibility of a covalent compound forming. In these cases the metal will travel as the original complex unless there is a compound in the solvent capable of forming a more stable bond with the metal ion.

Particular care should therefore be taken that the composition of the metal solution is the same under all conditions. It may be better in some cases to form the metal into the complex it is intended to measure before chromatograming the solution.

Where the conditions of concentration holding on the paper can be determined, a chromatographic method exists for studying the relative stability of complexes and also the exchange of ligands, occurring between complexes.

SUMMARY

The R_F values of the halides and tartrate of antimony have been determined using differing butanol-halide acid-water solvents. From the results obtained it has been concluded that the anion of the metal solution plays an important part in the R_F value of some metal ions. Possible extensions of the chromatographic method are suggested.

RÉSUMÉ

Les valeurs de R_F des halogénures et du tartrate d'antimoine ont été déterminées en utilisant différents solvants: butanol-acide halogénhydrique-eau. Des résultats obtenus, on a pu conclure que l'anion de la solution joue un rôle important sur la valeur de R_F de quelques ions métalliques. Des extensions possibles de la méthode chromatographique sont suggérées.

ZUSAMMENFASSUNG

Die R_F-Werte der Halogenide und des Antimontartrats wurden unter Verwendung verschiedener Lösungsmittel, wie Butanol-Halogenwasserstoffsäure-Wasser, bestimmt. Aus den erhaltenen Resultaten konnte man schliessen, dass das Anion der Lösung eine wichtige Rolle in Bezug auf den R_F-Wert einiger Metallionen spielt. Es wird zu möglichen Ausdehnungen der chromatographischen Methode angeregt.

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THE SELECTIVITY OF THE STATIONARY LIQUID IN VAPOUR PHASE CHROMATOGRAPHY

by

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INTRODUCTION

Gas-liquid partition chromatography, also known as Vapour Phase Chromatography (VPC), was introduced as an analytical method for the separation of fatty acids by JAMES AND MARTIN[1] in 1952. A separation of this kind is effected in a column packed with a solid porous material, the latter being impregnated with a non-volatile solvent, the stationary liquid. Small volumes (0.02-0.05 ml) of volatile compounds are carried through the column by a current of inert gas; changes in the composition of the gas issuing from the column are measured. The rate at which a volatile substance travels through the column depends on the vapour pressure above its solution in the non-volatile solvent. Components of a mixture of volatile substances will in general exert different vapour pressures above the solvent and will therefore travel through the column at different speeds, emerging from it separately in the inert gas stream.

The solvent used by JAMES AND MARTIN in the separation of fatty acids consisted of DC 550 silicone containing 10% of stearic acid. For the separation of amines and pyridines these authors used mixtures of hendecanol and liquid paraffin[2]. The order of elution of ammonia, mono-, di- and trimethylamine could be influenced by a change in the ratio of hendecanol to liquid paraffin. Whilst in their first paper it is said that "the separations obtainable by this method are essentially parallel to those obtainable by distillation . . .", the second paper clearly shows that the authors recognize the influence of the stationary liquid and that a comparison with extractive distillation is more appropriate.

As an analytical method the latter has never become an important tool, because it involves complicated operations. One of the great merits of VPC is that it allows of a simple application of the principle of extractive distillation.

RAY[5] tested several liquids as the stationary solvent and suggested the use of di (3.5.5 trimethylhexyl)phthalate (dinonyl phthalate or DNP) as a liquid of general applicability. In our work we also found that this ester is a very versatile stationary liquid, and its use can be recommended in numerous analytical separation problems. It should, however, be noted that the examples cited by RAY mainly deal with the separation of components in a series of homologues, and in such cases it is not necessary to make use of selective properties, such as the hydrogen bonding power of the stationary liquid. The separations effected by RAY are essentially also obtainable by sharp rectification; little or no use is made by him of the extractive properties of the stationary liquid in the VPC technique. It is this aspect which will be discussed.

THEORETICAL PART

When a mixture of substances is to be separated by vapour phase chromatography, the order of elution depends on the Henry coefficient K of the substances. (Henry's law states that the fugacity of a solute in dilute solution is proportional to its molar fraction; the proportionality factor, K, is the Henry coefficient.) The order will always be that of the vapour pressures of the pure substances if the components and the stationary liquid form an ideal solution. In this case it can readily be shown that the system obeys Raoult's law. Ideal solutions are more closely realized the more molecular species of solvent and solute are alike in their attractive forces; in the ideal case the kinetic energy required for the solute to escape from the solvent is the same as that needed for it to escape from its own pure liquid. Approximately ideal solutions are formed by certain pairs of non-associated liquids, such as the normal paraffins, and also by closely related associated liquids such as methanol and ethanol.

In vapour phase chromatography ideal solutions are rare, as the stationary phase must have a very low volatility, and the components to be separated must be volatile. If, for example, hexadecane is used as the stationary liquid for the separation of *n*-butane and *n*-pentane, distinct deviations from Raoult's law are encountered; the hexadecane molecules are arranged in approximately parallel array, and the molecules of the solutes do not depart very much from spherical symmetry. Consequently the molecular species of solvent and solute are not sufficiently alike, even though they are paraffins of different molecular weight, and the deviation from the ideal is caused by a non-ideal entropy of mixing. Without ignoring the influence of entropy, we believe that a qualitative picture of the factors that determine the selectivity of a liquid in the separation of volatile compounds can be obtained by considering the energetic aspect only.

In VPC we usually deal with solutions sufficiently dilute for Henry's law to apply; in other words the solute molecules are seldom sufficiently close together to influence each other. The direct environment of each solute molecule is nearly constant, although different in most cases from what it would be if it were surrounded by its own species; the volatility of the solute is mainly determined by the intermolecular forces between the molecules of solute and solvent, and no longer by the intermolecular forces between the molecules of the pure solute. The ratio of the vapour pressures of two solutes A and B will deviate from that of the pure substances when the intermolecular forces between A and the solvent are different from those between B and the solvent.

If we denote the vapour pressures of the pure substances A and B by p_A and p_B, and the Henry coefficient of the solutes A and B in the stationary liquid by K_A and K_B, p_A/p_B and K_A/K_B are a measure of the ease with which two components A and B may be separated from a mixture by rectification or by vapour phase chromatography respectively.

If $\frac{p_A}{p_B}$ is very close to unity, separation by normal atmospheric rectification is not possible; by the choice of a suitable stationary liquid, the vapour pressure of these components above this liquid may frequently be influenced to a different extent and $\frac{K_A}{K_B}$ may differ so far from unity that separation with the aid of VPC is easy. On the other hand it may occur that $\frac{p_A}{p_B}$ differs considerably from unity but $\frac{K_A}{K_B}$ is nearly 1, in which case the components A and B will coincide in VPC. This difficulty may, however, be overcome; the point will be discussed in the experimental part (see page 366).

Intermolecular forces

The difference in escaping tendency between two solutes A and B in the stationary liquid S is determined by the forces and energy of interaction between the molecules of A and S, and B and S respectively, provided that the solution is so dilute that the interaction between the A molecules and between the B molecules respectively is negligible. It is useful to recognize the different types of intermolecular forces which play a role in VPC and keep the molecules in the liquid state (cohesive forces)*:

(a) Forces between permanent dipoles of solute and solvent;
(b) Forces between a permanent dipole either of solute or solvent and the induced dipole of the other;
(c) Non-polar forces between solute and solvent molecules.

In the same order they have been designated by the terms orientation (KEESOM) forces, induction (DEBYE) forces and dispersion (LONDON) forces. The van der Waals forces are the sum of these three.

(a) If μ_A and μ_S are the permanent dipoles of solute and solvent molecules respectively, and r the distance between these dipoles, the polar axis being the line between their centres, KEESOM[4], by applying Boltzmann statistics, derived the following expression for the average potential energy between two dipoles

$$\bar{\varepsilon}_a = -\frac{2}{3}\frac{\mu_A{}^2\mu_S{}^2}{r^6 \cdot kT}$$

It is important to note that, with increasing temperature, the attraction energy caused by the forces of orientation decreases, and at very high temperatures, when all the orientations are equally probable, tends to become zero.

(b) The interaction energy resulting from the attraction between a permanent dipole and the moments induced by this dipole is expressed by the DEBYE formula

$$\bar{\varepsilon}_b = -\frac{1}{r^6}\,(a_S\mu_A{}^2 + a_A\ \mu_S{}^2)$$

The permanent dipole μ_A produces a field strength $F \sim \mu_A/r^3$. This field produces an induced dipole $\mu_i = \alpha F$, where α is the polarizability of the relative molecule. The energy $\varepsilon = -\frac{1}{2}\alpha F^2$ which is proportional to $-\frac{1}{2}\frac{\alpha\,\mu_i{}^2}{r^6}$. The induced energy is independent of temperature.

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* See also J. H. HILDEBRAND and R. L. SCOTT, *The Solubility of Nonelectrolytes*, 3rd edition, A. C. S. Monograph series No 17., Reinhold Pub. Corp.

(c) An expression for the potential energy between non-polar molecules has been derived by LONDON. For a better understanding of the dispersion or LONDON forces it is useful to consider a non-polar molecule as a rapidly varying dipole producing an electric field which acts upon the polarizability of the other molecule, and produces an induced dipole in phase with the first. The attraction energy was derived by LONDON as

$$\bar{\varepsilon}_c = -\frac{3\alpha_A\,\alpha_S}{2\,r^6} \cdot \frac{h\,\nu_{oA} \times h\,\nu_{oS}}{h\,\nu_{oA} + h\,\nu_{oS}}$$

where ν_o refers to the characteristic frequency of a molecule corresponding to its zero point energy.

The contribution of each of these three constituents to the total van der Waals forces may be estimated from those of some pure substances. The expressions for $\bar{\varepsilon}_a$, ε_b and $\bar{\varepsilon}_c$ apply to similar, as well as to dissimilar molecules. For similar molecules $\alpha_A = \alpha_S$, $\mu_A = \mu_S$ and $\nu_{oA} = \nu_{oS}$. The contribution to the total van der Waals attraction energy of each of the three types in pure substances can be seen from Table I, which has been taken from KETELAAR[4].

TABLE I

LATTICE ENERGY IN KCAL/MOLE, ACCORDING TO ORIGIN

	μ(in D)	α in cm³	KEESOM	DEBYE	LONDON	*Total*
A	0	1.63×10^{-24}	0.000	0.000	2.03	2.03
CO	0.12	1.99	0.0001	0.002	2.09	2.09
HI	0.38	5.40	0.006	0.027	6.18	6.21
HBr	0.78	3.58	0.164	0.120	5.24	5.52
HCl	1.03	2.63	0.79	0.24	4.02	5.05
NH_3	1.50	2.21	3.18	0.37	3.52	7.07
H_2O	1.84	1.48	8.69	0.46	2.15	11.30

The DEBYE energy is always small as compared with the KEESOM and LONDON energy. Nevertheless it would be wrong to neglect its influence in the separation of organic compounds.

It may happen that for two substances the total van der Waals forces are about equal, as for example in the case of the two closely similar compounds butene-1 (b.pt. —6.3° C) and *iso*butene (—6.9° C). The difference in volatility of these substances is so small that separation by rectification must be considered practically impossible. In VPC the task of the stationary liquid is to create a significant difference in volatility between dissolved butene-1 and dissolved *iso*butene; use must be made of the difference in structure between *iso*butene and 1-butene in such a way that one of these is attracted selectively by the molecules of the stationary liquid.

In the dissolved state the volatility of butene-1 (*A*) and *iso*butene (*B*) above the solvent (S) are determined by $\varepsilon_a{}^{A\text{-}S}$, $\varepsilon_b{}^{A\text{-}S}$, $\varepsilon_c{}^{A\text{-}S}$ and $\varepsilon_a{}^{B\text{-}S}$, $\varepsilon_b{}^{B\text{-}S}$, $\varepsilon_c{}^{B\text{-}S}$ respectively and the difference in volatility by

$$\Sigma\varepsilon^{A\text{-}S} - \Sigma\varepsilon^{B\text{-}S}$$

It may occur that ε_a and ε_c are almost equal for the system A-S and B-S but that $\varepsilon_b{}^{A\text{-}S}$ and $\varepsilon_b{}^{B\text{-}S}$, however small as compared with ε_a and ε_c, differ from each other and that the difference in the interaction energies is mainly determined by $\varepsilon_b{}^{A\text{-}S} - \varepsilon_b{}^{B\text{-}S}$; this signifies that the separation is essentially based on the difference in polarizability of the molecules A and B.

In the above, only forces and energies of attraction have been considered. The attractive forces are in balance with the repulsive forces, which set in fairly suddenly at small distances. The repulsive energy is proportional to a high inverse power of r (approximately the 12th power); the total potential energy of a molecular pair is then

$$\varepsilon = j/r^n - k/r^6 \qquad (n \text{ being } 12).$$

Compared with the energies playing a role in the production of stable chemical compounds, the cohesive energy is small. There are, however, dipoles in which hydrogen is linked to (C), N, O, which exert effects upon each other far beyond those expected from the dipoles alone. The reason for this phenomenon is that the bare proton of compounds with strongly negative atoms is so small that it can come very close to a second negative atom forming a "hydrogen bond". The exceptional nature of this bond is due to the closeness of approach of the two dipoles, which is rendered possible by the small size of the proton. The effect of this condition upon the total attractive energy is considerable, as in all the constituents of the total attractive energy the distance r appears as the inverse sixth power. The strength of the bond roughly falls off in the order F-H-F, O-H-O, N-H-N, C-H-O. Phenomena such as association and solvation are the result of hydrogen bonding. The energy of hydrogen bonding lies somewhere between that of the chemical bond and the normal cohesive energy.

The considerations given above demonstrate how the molecules of the stationary liquid in VPC influence the field around the dissolved molecules: liquids with low internal pressure, such as non-polar liquids, have a weak field; liquids with high internal pressure have a strong field and may exert strong attractive forces on the dissolved molecules.

The theory of solutions is still far from accurate and we are not in a position to predict the separation given by a solvent from the properties of the solvent and those of the components to be separated. But if one wishes to select a liquid out of several promising solvents or to narrow down the list of possible ones, the above considerations may be of assistance.

The kind of effects to which changes in the type of stationary liquid can give rise will be shown in a few examples, which have been taken from an extensive field of analytical applications.

EXPERIMENTAL PART

Apparatus and procedure

We shall dispense with a detailed description of our apparatus and procedure which are very similar to those used by RAY[5]. The packing of the chromatographic column consisted of either Celite 545 or of Sterchamol, a furnace insulation brick, ground to a particle size of 30-100 mesh.

Sterchamol is a macroporous material and compares with Celite in that it is capable of supporting at least an equal amount of the stationary liquid. The main advantages of Sterchamol are that high gas-flow rates can be obtained with a relatively low drop in pressure, and that the chromatographic column can be filled reproducibly. The latter fact is due to the sandy nature of the material even when it supports about 40% of its weight of the stationary solvent. Homogeneous distribution of the stationary liquid was effected by diluting it with *n*-pentane or diethyl ether and subsequently evaporating the diluent.

Detection

In many cases the carrier gas emerging from the column contains only one of the volatile components at a time, and the method of detection can therefore be simple.

A) *Differential method.* A plot of the concentration of a component in the effluent versus the amount of effluent shows a curve approaching the Gaussian (or normal error) curve. A method by which the instantaneous concentrations of the components in the effluent are measured yields a series of Gaussian curves. The instantaneous concentrations can be measured, for instance, by means of thermal conductivity; the rapid changes are registered with an automatic recording millivolt meter. The separation between two components is complete if the recorder returns to its base line between two successive Gaussian curves; this signifies that pure carrier gas is issuing from the column at that moment.

B) *Integral method.* If the volatile components leaving the column are separated from the carrier gas and are then collected, the total amount of these components can be measured at each moment. This may also be automatically recorded; the result is now a series of sigmoid curves. There is a complete separation if a portion of the curve is parallel to the base line between two sigmoids.

Separation of components from the carrier gas can be effected either

1. by removal of this gas (*e.g.* of CO_2 by absorption in caustic) or
2. by absorption of the components (*e.g.* fatty acids in caustic, amines in an HCl solution).

When VPC is used as an analytical tool, the "integral" method has distinct advantages over the "differential" one, especially for the quantitative determination of a number of components in a mixture, as it does not require calibration. For the determination of impurities in "pure" substances, however, the "differential" method is preferable because of its higher sensitivity.

The investigation to be described below mainly deals with the question of whether two components can be separated from each other; the discussion given here is confined to the qualitative aspect. In this case the detection method by the differential technique, using thermal conductivity, proved to be convenient.

Examples

1. Separation of hydrocarbon gases; analysis of a C_4 hydrocarbon gas

Let us consider as an example the case of a C_4 hydrocarbon gas containing C_3 admixtures. The gas, if obtained from cracking gases in the petroleum industry, may contain the following main components in the percentages shown:

Component	*Boiling point, °C*	*mol.%*
Propene	—47	2
Propane	—42.1	11
*iso*butane	—11.7	16
*iso*butene	— 6.9	16
Butene-1	— 6.3	16
n-butane	— 0.5	27
trans butene-2	+ 0.9	6
cis butene-2	+ 3.7	6

The separation of these components has been studied at the temperature of melting ice, and five different stationary liquids have been used, *viz.*,

a. a hydrocarbon oil (a transformer oil with average mol wt 310);
b. dinonyl phthalate, *i.e.*, di(3.5.5-trimethylhexyl)phthalate, mol wt 418;
(The alcohol used for the preparation of this ester is at present commercially available. The alcohol was prepared from di-*iso*butene by the oxo-synthesis.)
c. di *n*-butyl phthalate, mol wt 256;
d. ethyl acetoacetate, ,, ,, 130;
e. dimethyl formamide, ,, ,, 73.

The separations were carried out in a column of 1800 mm length and 6 mm internal diameter. N_2 was the stripper gas; the pressure at the outlet was atmospheric and the pressure drop over the column 80 mm; gas velocity, 2 l/h. Sterchamol 30-100 mesh was used as the support for the stationary liquid and contained 40 grams of the latter per 100 grams of support. The column contained in each case 8 grams of stationary liquid, *i.e.* 0.026, 0.019, 0.031, 0.062 and 0.110 moles for the various stationary liquids respectively. In Figs. 1a-e the elution curves obtained by thermal conductivity measurements, registered on a Brown-Honeywell recorder, are shown; they should be read from right to left.

1a. *Stationary liquid: transformer oil*

This is a liquid with very low internal pressure; it is not polar and the attractive interaction energy is of the LONDON-type exclusively. The order in which the components issue from the column is that of the boiling points. There is no paraffin-olefin selectivity. There is no separation between butene-1 and *iso*butene, which have boiling points lying very close together. The separation between *n*-butane and the two butenes-2 is very poor, as might be expected from the differences in boiling points. The presence of propene shows up as a deformation at the base of the propane peak.

1b. *Dinonyl phthalate*

This is a polar liquid and the molecules produce an electric field and polarize the solute molecules. The polarizability of olefins is somewhat higher than that of the paraffins, and consequently the total attractive energies will be higher for the olefins than for the paraffins. As a result the escaping tendency of the butenes, and thus the vapour pressure, is lowered, and we see that in the elution diagram butane coincides with the lower-boiling butene-1 and *iso*butene. Moreover, the retention volume (which is measured as the distance from the injection point I to the point of intersection T between base line and the inflection tangent of the downcoming part of the butane elution curve; IT in Fig. 1b) of the butenes-2 is increased. Propene coincides with propane.

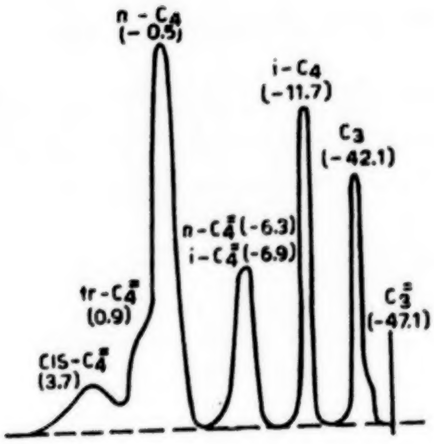

Fig. 1a. Transformer oil

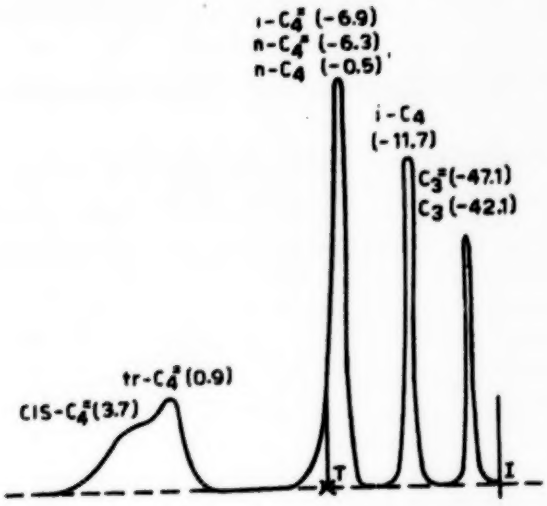

Fig. 1b. Dinonyl phthalate (DNP)

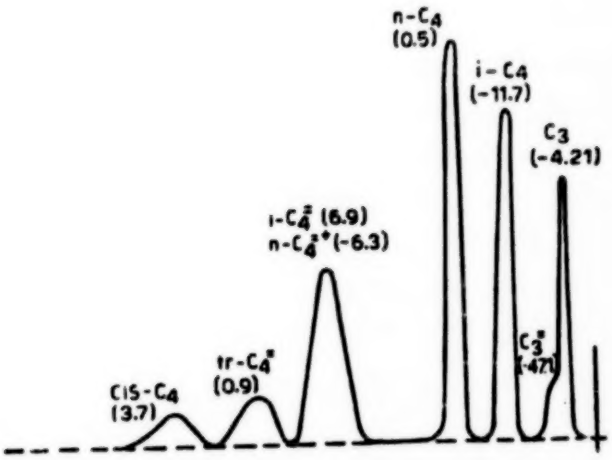

Fig. 1c. Dibutyl phthalate (DBP)

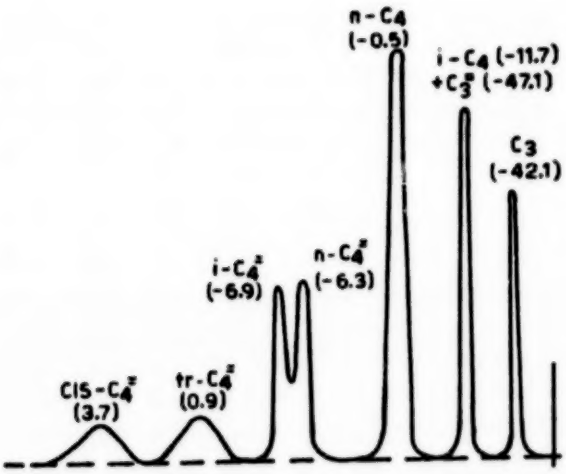

Fig. 1d. Ethyl acetoacetate (EAA)

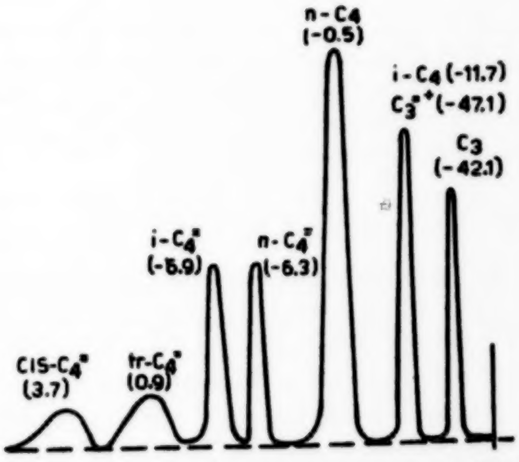

Fig. 1e. Dimethyl formamide (DMF)

Fig. 1 Separation of a C_4 hydrocarbon gas over various stationary liquids
Experimental conditions:
Column: Length 6′
I.D. $^1/_4$″
Support Sterchamol 30-100 mesh
Liquid/support 40/100 W
Temperature 0° C
Outlet pressure 1 atm.
Gas N_2 2000 ml/h

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1c. *Dibutyl phthalate* (DBP)

This liquid is similar to dinonyl phthalate, but the molecules are of a smaller size, and the distance between the molecules of solute and solvent will therefore also be smaller than in the previous case. The effect of *r* on the attractive energies is considerable, so that it is not surprising that the selective decrease in vapour pressure of the olefins observed with dinonyl phthalate is more pronounced with dibutyl phthalate. Butene-1 and *iso*butene (which coincide with *n*-butane in the case of dinonyl phthalate) are now separated from *n*-butane and issue after it from the column. The separation between *cis* and *trans* butene-2, already indicated by the shape of the elution curve in Fig. 1b, is now complete. The improved separation must certainly be partly ascribed to the fact that the dibutyl phthalate column contains more moles of the stationary liquid, and therefore the number of stages of the column will be higher; this can explain the complete separation between *cis* and *trans* butene, but it cannot explain the separation of butane from $C_4^{=}$-1 and *iso* $C_4^{=}$, which coincided in the case of DNP (1b).

1d. *Ethyl acetoacetate* (EAA)

This ester has a keto and an enol configuration; these forms differ in the position of a proton and it is to be expected that the substance will exert a considerable hydrogen bonding power. The tendency of the Henry coefficient to decrease selectively for the olefins is continued. The elution curves in Fig. 1d show that a fair, though not a complete, separation is obtained between *iso*butene (b.pt. —6.9° C) and butene-1 (b.pt. —6.3° C) and that the order of elution is the reverse of what would be expected from the volatility of the pure substances. This is a good example of how the separation between two very similar compounds, for which the vapour pressures of the pure substances are about equal, becomes possible by a proper choice of stationary liquid. For the pure substances the volatility of *iso*butene is somewhat higher than that of butene-1. The polarizability of *iso*butene, however, is larger than that of butene-1 which signifies that for *iso*butene the Debye and the London terms in the attraction energies will be larger than for butene-1. This is partly counteracted by the Keesom term, which is higher for butene-1, as it has a permanent dipole of 0.3 D, whereas *iso*butene has no dipole. Obviously the result is that the Debye and London terms predominate, eventually making butene-1 the more volatile component. It is also possible that the spherical symmetry of *iso*butene will cause the distance *r* between solute and solvent to be smaller than for the more linear butene-1, and as a result, the attractive energy between solute and solvent molecules will be higher for *iso*butene.

It should be observed that with ethyl acetoacetate, propene (b.pt. —47° C) coincides with *iso*butane (b.pt. —11.7° C), instead of with propane as in the previous examples 1a, 1b and 1c.

1e. *Dimethyl formamide* (DMF)

The main advantage of this liquid over ethyl acetoacetate probably lies in its low molecular weight which causes the molar density of the liquid in the column to become higher, so that the number of stages is also higher. It cannot be said that dimethyl formamide has a higher selectivity than ethyl acetoacetate; Figs. 1e and 1d are very similar, propene and *iso*butane coinciding in both cases. The complete separation of butene-1 and *iso*butene may be ascribed to the higher number of stages of the dimethylformamide column.

The stationary liquids just described have an increasing selectivity for the separation of olefins and paraffins. In the diagrams there is a gradually increasing tendency for the paraffins to shift to the right and for the olefins to shift to the left of the diagram*. The liquids did not allow of a complete separation between all components of a C_4 gas containing small amounts of C_3. Stationary liquids permitting a separation of *iso*butene and butene-1 will not separate propene from *iso*butane. To overcome this difficulty, two columns in series may be used. In the first column a non-polar liquid is employed, and the components are separated in the order of their boiling points. In the second column the components are separated according to their functional groups by a strongly polar liquid such as dimethyl formamide. Consequently the moment of introduction of *iso*butane (b.pt. —11.7° C) into the second column is retarded with respect to propene (b.pt. —47° C). It is obvious that there must be a good balance between the dimensions of the two columns, and that the separations obtained in the first column must be maintained in the second.

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* It should be noted that the time axis in the diagrams is different. The diagrams have been so drawn that the retention time of *iso*butane is represented by the same interval.

The relatively high volatility of ethyl acetoacetate and dimethylformamide renders these stationary liquids less suitable for the separation of higher-boiling hydrocarbons.

2. *Separation of saturates from aromatics*

The following example involves the analysis of products obtained by catalytic reforming of naphtha fractions with the aid of platinum catalysts. Reforming is carried out under H_2 pressure and the reaction products, which are practically free of olefins, consist of saturates (paraffins and naphthenes) and aromatics. An accurate analysis by VPC of the aromatics in such reformed products, which usually have a fairly wide boiling range, is often hampered by total or partial coincidence of the peaks for the aromatics with those of the paraffins or naphthenes of higher boiling point, such as in the case of benzene (80° C) with the isoheptanes (90° C). It has been found that even with stationary liquids of very low internal pressure, for instance a liquid paraffin, the retention of an aromatic is somewhat higher than that of a paraffin of the same boiling point.

There are two ways of overcoming this difficulty. Let us consider for example a reformed product with a boiling range of 60°-145° C (obtained by reforming a 90°-135° C naphtha).

The product contains (C_6-C_9) paraffins and isoparaffins, C_6-C_8 naphthenes and the aromatics benzene, toluene, ethylbenzene, *m*-, *o*- and *p*-xylene. If this reformed product is split up into fractions of suffiently narrow boiling range, each fraction may be analysed by VPC, and the aromatics can be determined accurately.

A more attractive way is to carry out a preliminary separation between the aromatics and saturates by means of liquid phase adsorption chromatography over silica gel. The aromatics obtained in this way can then be analysed accurately by VPC. As will now be shown, it has proved possible to find a stationary liquid with which the aromatics in the full range 60-145° product can be analysed without any pre-separation. This study has been carried out with a blend obtained by mixing:

acetone	2%
n-octane	8%
*iso*nonane (methyl branched)	2%
benzene	8%
toluene	8%
ethyl benzene	18%
o + *m* + *p*-xylene	18 + 18 + 18%

Acetone was added as a marker (or internal standard). It is used in the estimation of the amount of the various components.

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Among the non-volatile liquids examined, four are mentioned here: transformer oil, DNP, DNP + picric acid (65 : 35 wt) and the addition compound of fluorene and picric acid (1 : 1 molar).

The experimental conditions were the same as those employed in the previous example, except for the column temperature which was 120° C; the thermal conductivity cell was also operated at elevated temperature. The elution curves obtained are shown in Figs. 2a-d.

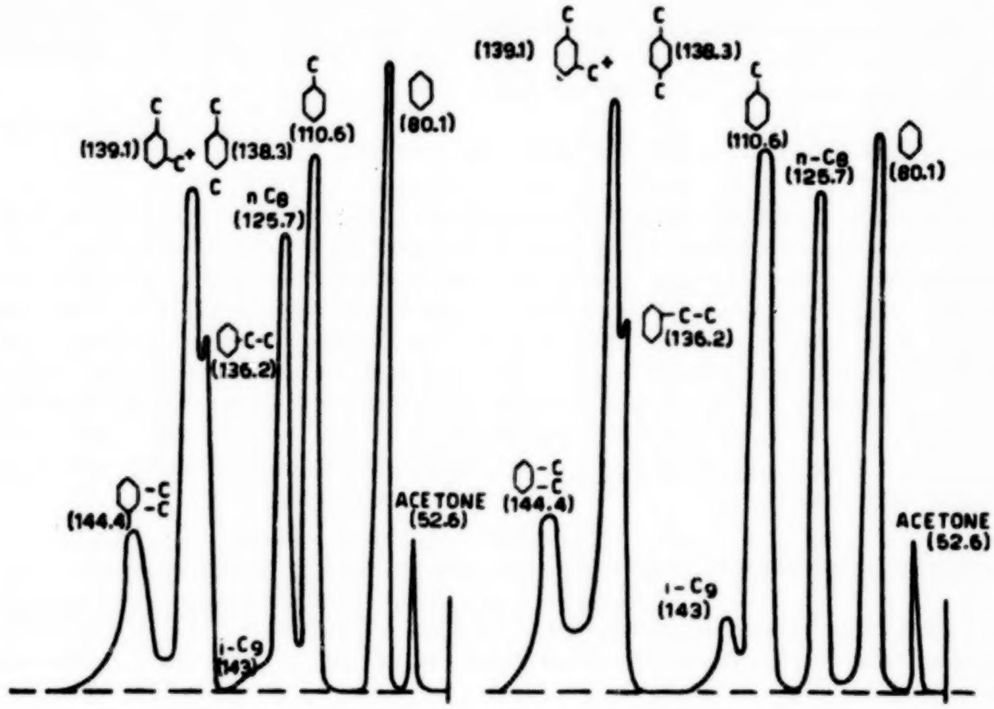

Fig. 2a. Transformer oil Fig. 2b. Dinonyl phthalate (DNP)

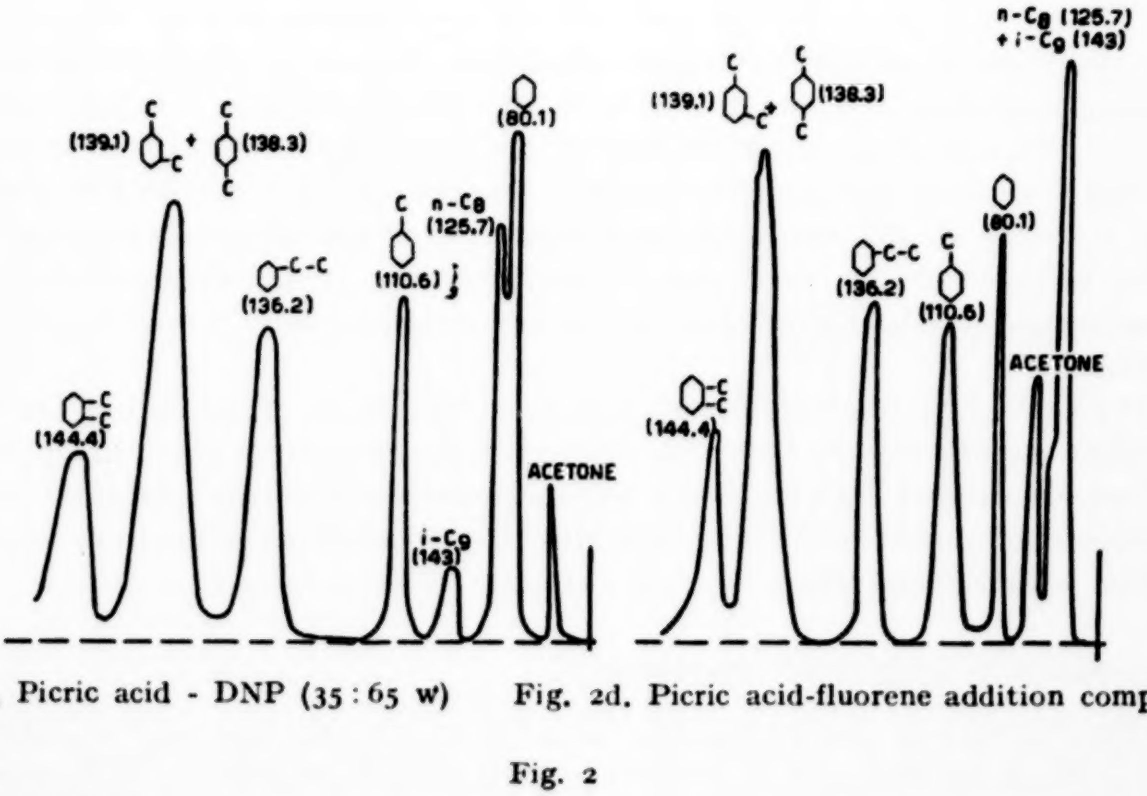

Fig. 2c. Picric acid - DNP (35 : 65 w) Fig. 2d. Picric acid-fluorene addition compound

Fig. 2

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2a. *Transformer oil*

The diagram shows that the order of elution is almost that of the boiling points of the components, acetone, benzene, toluene *n*-octane + *iso*nonane, ethylbenzene + *m* + *p*-xylene and *o*-xylene. Between *n*-octane and the C_8 aromatics there is an indication of the presence of *iso*nonane. The separation of ethylbenzene from *m* + *p*-xylene is very poor; *m* + *p*-xylene show up as one component. This behaviour is in accordance with that expected for a stationary liquid of low internal pressure.

2b. *Dinonyl phthalate* (DNP)

This liquid shows some selectivity for aromatics, *n*-octane (b.pt. 125.7° C) emerges from the column before toluene (b.pt. 110° C) and *iso*nonane before the C_8 aromatics. Again the separation between ethylbenzene and *m* + *p*-xylene is poor.

2c. *Picric acid dissolved in dinonyl phthalate* (35 : 65 wt)

Picric acid alone is not suitable as a stationary liquid; at its melting point (122° C) it is already too volatile. It is soluble and less volatile in DNP and it has been employed as a 35 : 65 wt solution at temperatures up to 125° C. With picric acid the effect of the hydrogen bonding power is again observed. The saturates have a much larger escaping tendency than the aromatics; *n*-octane emerges from the column immediately after benzene; these components nearly coincide, though the difference in boiling point is 45° C. In the same way *iso*nonane appears before toluene, from which it is completely separated. The most striking difference compared with 2b, however, is that ethylbenzene is now completely separated from *m* + *p*-xylene. With this stationary liquid there are two kinds of selectivity: a saturates-aromatic selectivity and a selectivity for certain aromatic individuals.

2d. *Picric acid-fluorene addition compound*

Picric acid forms a molecular addition compound with fluorene (1 : 1); the addition compound has a melting point of 80° C and starts to decompose at 130° C. At 125° C it has a sufficiently long lifetime.

Fig. 2d shows that if this addition compound is used as the stationary liquid the aromatics-saturates selectivity is complete. The attractive forces between the molecules of the stationary liquid and those of the paraffins are very weak so separation between the paraffinic molecules will be very poor. The diagram (Fig. 2d) shows that *n*-octane and *iso*nonane emerge from the column even before acetone. The shoulder in the descending part of the octane peak just shows the presence of *iso*nonane.

A rapid method of analysis of the aromatics present in products obtained by reforming naphthas is of great benefit in the development of catalytic reforming processes. Vapour phase chromatography is such a rapid method, and it has been seen that the picric acid-fluorene addition compound is a very selective stationary liquid, not only for the separation of aromatics from the saturates, but also for the analysis of the individual aromatics at the same time. It should be noted that with the stationary liquids studied thus far, no separation between *m* and *p*-xylene could be effected.

In the above example naphthenes have been left out of consideration. On the one hand these naphthenes are converted to a very large extent into aromatics if platinum catalysts are used in reforming and will be present in low concentrations only. On the other hand naphthenes, being saturates, are expected to emerge from the column together with the paraffins.

3. *Separation of oxygenated compounds*

In the preparation of *iso*propyl alcohol (IPA) by hydration of propene, di*iso*propyl ether (IPE) is formed as a by-product; in the dehydrogenation of IPA to acetone, unconverted IPA will be an impurity in acetone, whereas acetone in its turn can be considered as an impurity in the unconverted IPA used for recycling. A means of analysing such mixtures is clearly of importance.

3a. *Dinonyl phthalate*

The first stationary liquid tried out was dinonyl phthalate, proposed by Ray. It appeared, however, that the separation between acetone and IPE is very poor and that IPE and IPA are not separated at all. This might be considered rather surprising, as the boiling points are: acetone 56.1° C, IPE 68.4° C and IPA 82.3° C, and separation by rectification does not offer insuperable difficulties.

3b. *C_{27} paraffins*

Therefore, the next liquid tried out was one with very low internal pressure, a C_{27}-paraffin. It was expected that, as with the transformer oil used in the previous examples, the paraffin would effect a separation according to the boiling point. However acetone and *iso*propanol showed up as one peak, so that obviously the lowest and the highest boiling component have the same volatility in this paraffin. This must be ascribed to a dissociation of associated *iso*propanol molecules, due to the dilution by the solvent; the effect will increase the escaping tendency of IPA. In agreement with this view, the retention volume of IPE is larger than that of acetone and IPA, so that the relative volatility of IPA is selectively increased.

3c. *Octadecanol*

On the basis of the maxim "*similia, similibus solvuntur*", a high boiling alcohol was chosen as stationary liquid, *viz.* octadecanol. This alcohol actually gave a good separation and the order of elution was that of the boiling points of the components.

3d. *Diglycerol*

The encouraging results obtained with octadecanol led us to test a polyalcohol. Diglycerol $(CH_2OH\text{-}CHOH\text{-}CH_2)_2\text{-}O$ was chosen because of its very low volatility and good thermostability. This ether is obtained by dehydration of glycerol. It appeared to be a very powerful and selective liquid. The elution curves obtained in the separation of acetone, IPE and IPA at 56° C are shown in Fig. 3. For the quantitative determination of these components use has been made of benzene as an internal standard ("marker"). The order of elution is not that of the boiling points but: IPE (68.4° C), acetone (56.2° C), IPA (82.3° C).

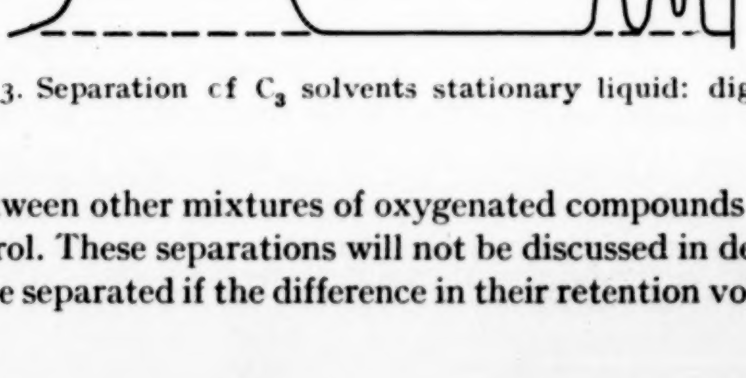

Fig. 3. Separation of C_3 solvents stationary liquid: diglycerol

Separations between other mixtures of oxygenated compounds are also possible by the use of diglycerol. These separations will not be discussed in detail. In general two components can be separated if the difference in their retention volumes is sufficiently large. Therefore, the R.V.'s have been measured for a number of pure substances. In all cases the measurements were carried out with the aid of a standard substance, for which IPA was arbitrarily chosen. If the peaks for IPA and the relative substance coincided, another suitable standard was chosen. In this way a number of R.V.'s relative to the R.V. of IPA was obtained; they are listed in Table II, not only for the stationary liquid diglycerol, but also for DNP and partly for octadecanol and C_{27}-paraffin. It should be noted that a comparison of R.V.'s is allowable only within the columns of Table II and not between them, because in each column the R.V. of IPA is assigned a value of unity.

Table III has been extracted from Table II, but whilst in the latter the volatile substances have been arranged in the order of boiling points, they have been listed in Table III according to the functional groups.

TABLE II

RETENTION VOLUMES OF OXYGENATED COMPOUNDS RELATIVE TO THAT OF *iso*PROPANOL IN VARIOUS STATIONARY LIQUIDS

Solute *Stationary liquid*	*Boiling point*	*Diglycerol*	*DNP**	*Octadecanol*	*C_{27} paraffins*
Acrolein	52.5	0.25	0.84	—	—
Acetone	56.1	0.28	0.90	0.40	1
Methanol	64.7	1.40	0.56	—	—
Di-*iso*propyl ether	68.4	0.08	1.02	0.68	1.36
Ethanol	78.3	1.27	0.82	—	—
Methyl ethyl ketone	79.6	0.30	1.54	—	—
*iso*Propanol	82.3	1.00	1.00	1.00	1.00
Tertiary butanol	82.5	0.74	1.17	—	—
Allyl alcohol	97.0	2.86	1.50	—	—
Propanol	97.2	1.68	1.64	—	—
Sec. butanol	99.5	1.22	1.82	—	—
*iso*Butanol	108.1	1.54	2.60	—	—
Methyl-*iso*butyl ketone	115.9	0.35	4.3	0.91	3.60
n-Butanol	118	2.88	3.56	—	—
Mesityl oxyde	129.5	1.20	5.40	1.51	7.12
Methyl-*iso*butyl carbinol	131.8	2.17	6.0	1.6	4.16
Diacetone alcohol	166	—	4.20	1.84	5.20
Benzene	80.8	0.16	2.02		

The retention volume of water in diglycerol relative to that of IPA is > 10.
* DNP = di-(3.5.5-trimethylhexyl) phthalate.

It will be seen that with diglycerol the ketones may be completely separated from the primary alcohols, but that with DNP *n*-propanol almost coincides with methyl ethyl ketone and ethanol with acetone.

With diglycerol the order of elution of the primary alcohols deviates from that of the boiling points, ethanol being more volatile than methanol. Probably this can be explained by the strong hydrophylic character of diglycerol. The hydrophylic character of the alcohols decreases in the order methanol, ethanol, propanol, and as a consequence the KEESOM orientation forces decrease in the same order. The orientation interaction energy is thus highest for methanol. The LONDON and perhaps also the

TABLE III

RETENTION VOLUMES OF SOME KETONES AND ALCOHOLS RELATIVE TO THAT OF IPA IN DIGLYCEROL AND DNP

	B.pt.	*R.V. in digl.*	*R.V. in DNP*
Acetone	56.1	0.28	0.90
Methyl ethyl ketone	79.6	0.30	1.54
Methyl *iso*butyl ketone	115.9	0.35	4.3
Methanol	64.7	1.40	0.56
Ethanol	78.3	1.27	0.82
Propanol	97.2	1.68	1.64
Butanol	118	2.88	3.56
IPA	82.3	1.00	1.00

DEBYE forces, however, *increase* in the same order and in the total interaction energy there is obviously a minimum for ethanol. With DNP, a substance with a more lipophylic character, all three constituents of the total van der Waals energy increase in the same order.

Other interesting applications may be derived from Table II. We shall here draw attention only to the difference in R.V. of allyl alcohol (b.pt. 97.0° C) and *n*-propanol (97.2° C) which have relative R.V.'s of 2.86 and 1.68 respectively, and thus are easily separated with diglycerol.

CONCLUSIONS

In the above it has been shown that the choice of the stationary liquid is a powerful experimental parameter in vapour phase chromatography. Though theoretical considerations help to narrow down the list of all possible liquids, the proper choice is often still a matter of trial and error. However, the work now proceeding in various laboratories will, no doubt, clarify the fundamental theory.

In the separation of hydrocarbon gases the use of dimethyl formamide makes the separation of α- and *iso*-butene possible.

With the picric acid-fluorene addition compound an accurate analysis of aromatics is possible in hydrocarbon fractions of fairly wide boiling range, no interference of the saturates present being encountered.

Diglycerol is a very useful liquid for the separation of oxygenated substances.

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SUMMARY

Vapour phase chromatography is a highly efficient analytical technique for the separation of gases and volatile liquids. The stationary phase in this percolation process is a liquid supported by an inert solid carrier material of a suitable particle size. The important role played by this liquid in the separation of a mixture into its components is discussed.

RÉSUMÉ

La chromatographie en phase vapeur est une technique très avantageuse pour la séparation analytique de gaz et de liquides volatiles. Dans cette technique, la phase stationnaire est un liquide, supporté par une substance solide à particules de grosseur appropriée. Le rôle important du liquide stationnaire dans la séparation des composants d'un mélange est discuté.

ZUSAMMENFASSUNG

Dampfphase-Chromatographie ist ein zweckmässiges Analyseverfahren zur Trennung von Gasen und flüchtigen Flüssigkeiten. Die stationäre Phase in diesem Prozess ist eine Flüssigkeit auf einem inaktiven festen Träger von geeigneter Korngrösse. Die wichtige Rolle dieser Flüssigkeit in der Trennung einer Mischung in ihre Bestandteile wird besprochen.

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DETERMINATION OF IMPURITIES IN TUNGSTEN METAL

I. DETERMINATION OF COPPER

by

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The method proposed in the A.S.T.M. *Methods for Chemical Analysis of Metals* for determination of copper in tungsten and ferro-tungsten involves solution of the tungsten in hydrofluoric acid/nitric acid mixture, removal of the hydrofluoric acid by sulphuric acid fuming, complexing the tungsten with tartaric acid and precipitation of the copper with hydrogen sulphide. After removal of Group IIb sulphides the copper sulphide is dissolved and copper determined electrolytically or volumetrically (iodide method).

There are a number of objections to the above procedure.

(a) It is of limited sensitivity, and unreliable below 0.01% copper.

(b) A large sample weight (5 g) is required.

(c) The procedure is rather tedious, especially for routine analysis.

The absorptiometric method described in this paper meets all of these objections.

A number of reagents are commonly used for absorptiometric determination of copper. Of these, sodium diethyldithiocarbamate is the most familiar, but a somewhat improved reagent is 2,9-dimethyl-1,10-phenanthroline ("neo-cuproine")[1,2]. Neocuproine is stated to be completely specific for copper (several elements react with sodium diethyldithiocarbamate[5]) and using a chloroform extraction technique we have found that the sensitivity (using the Spekker absorptiometer) is considerably greater than that of sodium diethyldithiocarbamate. HACKETT[6] has carried out a number of experiments using 2,2′ Diquinolyl[3] and it appears that this reagent could be used instead of neocuproine under exactly the same conditions, except that a different colour filter (Ilford Spectrum Green No. 604) would be required to measure the absorption. The sensitivity is slightly less, but of the same order.

The most efficient technique for using neocuproine is that described by GAHLER[2,4]. The pH of the solution is brought within the range 4 to 7, an alcoholic solution of neocuproine is added, and the yellow copper complex extracted with chloroform. Over 99% of the complex is removed by one extraction, so two extractions only are required for complete removal of the copper.

It is necessary to complex the tungsten, and we have found that if tungsten is converted to phosphotungstic acid (at the same time eliminating hydrofluoric acid) and then a little citrate is added to prevent hydrolysis, no tungsten precipitates at this pH range.

It is desirable for routine analysis to obtain a fixed pH without the use of a pH meter, and if 2 g sodium acetate are added for every 1 ml phosphoric acid the pH of the final solution is in the desired range.

Hydroxylamine hydrochloride was found to be satisfactory for reducing the copper to the cuprous form prior to complexing it.

None of the reagents used were completely copper-free and for accurate work a blank determination was desirable. A typical blank determination was equivalent to 0.0003% copper.

The method used is as follows:

Dissolve 1.0 g tungsten *(Note 1)* in 2 ml nitric acid and 2 ml hydrofluoric acid in a covered platinum basin. When dissolved remove the lid, rinse with a small quantity of water, add 2 ml phosphoric acid and evaporate to a syrup to eliminate nitric and hydrofluoric acid. To the cold residue add 25 ml 4% sodium citrate solution, stir to dissolve, cool, add 1 g hydroxylamine hydrochloride and 20 ml 20% sodium acetate solution. Transfer to a 100 ml separating funnel with water washings and add 10 ml 0.1% alcoholic solution of neocuproine (preferably ANALAR absolute ethyl alcohol). Leave 10 minutes, then add 10 ml ANALAR chloroform and shake for 1 minute. Allow to settle, and run off the chloroform layer into a 50 ml graduated flask. Repeat the extraction with a further 5 ml chloroform and combine the extracts. Dilute the extracts to 50 ml with alcohol. (This should then give a clear solution). Measure the absorption of the extract on the Spekker absorptiometer, using 4 cm cells, and Ilford Spectrum Violet filters No. 601, and a water/water setting of 1.0.

Note 1

The above method covers a range of copper content of 0 to 0.01%. If the copper is > 0.01% a smaller weight of tungsten should be taken.

To obtain the calibration curve a standard copper solution is prepared. Dissolve 0.1 g electrolytic copper (>99.9% copper) in 2 ml nitric acid and 5 ml water, evaporate the solution to dryness, take up the residue in 1 ml hydrochloric acid and dilute the solution to 100 ml. A dilute copper solution is then prepared by diluting 5 ml of the above solution to 500 ml, and this contains 10 µg Cu per ml. Take 0, 1, 2, 3 . . . 10 ml of this solution, and add 2 ml hydrochloric acid to each fraction, followed by sodium citrate, hydroxylamine hydrochloride *etc.* as in the method described.

Owing to the difficulty of obtaining tungsten free of copper, and in the absence of any standardized tungsten samples, the accuracy of the method was checked by first determining the copper content of a tungsten powder, and then adding a known quantity of standard copper solution to test the recovery — 100% recovery was obtained.

Table I gives the analyses of certain tungsten metal powders examined. The second column of figures were obtained by the General Electric Co., Research Laboratories using an (unpublished) polarographic method.

TABLE I

Sample	*Found by neocuproine method*	*Found by G.E.C. polarographic method*
WZ19	0.0013 %	0.0014 %
BB73	0.0025 %	0.0026 %
VAC 41	nil	nil
DZ187	0.0046 %	0.0044 %
VCC28	0.0021 %	0.0016 %
X2	0.0002 %	0.0004 %

Agreement between the two methods is very good.

Acknowledgement is due to Mr. M. L. ASPINAL for assistance in the experimental work, and to Mr. L. J. DAVIES, Director of Research, The British Thomson-Houston Co., for permission to publish this paper.

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SUMMARY

A method is proposed for the determination of copper present as an impurity in tungsten. 2,9-dimethyl-1,10-phenanthroline forms a stable complex with the cuprous ion, which can be extracted by chloroform (in presence of alcohol) from aqueous solution and determined absorptiometrically. Tungsten is complexed with citric acid and phosphoric acid.

RÉSUMÉ

Une méthode est proposée pour le dosage du cuivre, présent comme impureté dans un tungstène. La 2,9-diméthyl-1,10-phénanthroline forme avec les ions cuivre(I) un complexe stable pouvant être extrait par le chloroforme (en présence d'alcool) et dosé absorptiométriquement. Le tungstène est complexé par l'acide citrique et par l'acide phosphorique.

ZUSAMMENFASSUNG

Es wird eine Methode vorgeschlagen, um Kupfer zu bestimmen, welches sich als Verunreinigung in Wolfram befindet. Das 2,9-Dimethyl-1,10-phenanthrolin bildet mit den Kupfer(I)ionen einen stabilen Komplex, welcher mit Chloroform (in Gegenwart von Alkohol) ausgezogen und Absorptiometrisch bestimmt werden kann. Das Wolfram wird mit Zitronen- und Phosphorsäure komplexiert.

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DETERMINATION OF IMPURITIES IN TUNGSTEN METAL
II. DETERMINATION OF IRON

by

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The methods described in SMITHELLS' *Tungsten* for determination of iron are based on a prior separation of tungsten either (a) by volatilisation of tungsten as tungsten oxychloride or (b) a sodium hydroxide or sodium carbonate separation.

If small amounts of iron are present it is recommended that iron be estimated colorimetrically using thioglycollic acid or ammonium thiocyanate.

These methods are somewhat undesirable for very low iron contents because (a) a large sample weight is required (b) precipitation with sodium hydroxide and carbonate is not always complete at low iron concentrations.

Moreover these methods are tedious, and not very suitable for routine analysis.

In this paper an absorptiometric method is described, which is both more rapid and more sensitive than the methods described above.

The most sensitive reagent for iron at present available in this country is 4,7-diphenyl-1,10-phenanthroline[2,3] (known as bathophenanthroline). It has several advantages over the thiocyanate and thioglycollic acid complexes —

(a) It is completely specific (copper gives a coloured complex, but only at a pH >7).
(b) It is much more sensitive.
(c) The complex can be readily extracted with organic solvents.

In exploratory attempts to use this reagent a similar method to that described in Part I (DETERMINATION OF COPPER)[4] was used. This had to be abandoned for the following reasons:

(a) Phosphoric acid prevented the formation of the iron complex.
(b) In presence of citric acid, hydroxylamine hydrochloride did not give complete reduction of the ferric ion.

Other complexing agents, oxalic acid, tartaric acid and hydrofluoric acid were tried but in no case was complete reduction obtained with hydroxylamine. Other reducing agents tried were hydrazine hydrochloride, hydroquinone and sodium dithionite. Hydrazine hydrochloride was ineffective, hydroquinone gave a heavy blue coloration and precipitate with tungsten, as did sodium dithionite in presence of certain complexing agents, but not others.

After trying a number of combinations it appeared that the most promising was citric acid and sodium dithionite. It was necessary to neutralize with sodium hydroxide rather than ammonium hydroxide; otherwise there was a tendency for iron tungstate to be precipitated and low iron figures to be obtained.

The next problem was to reduce the reagent blank, which was equivalent to about 0.002 to 0.003% iron. The reagents were examined in turn, and the main sources of iron were found to be the sodium dithionite (0.0005%), the citric acid (0.0006%), and the sodium hydroxide (0.0003%) iron. These are purified as follows:

The sodium dithionite is prepared as a 10% solution immediately before it is required, and for every 50 ml solution, 10 ml of the reagent solution (0.05% 4,7-diphenyl-1,10-phenanthroline in alcohol) are added. It is then pre-extracted with two 10 ml portions of chloroform A.R. to remove the iron complex. (Sodium dithionite is unstable in solution, and should be used immediately after this pre-extraction).

The citric acid is prepared as a 10% solution. To 500 ml, 5 ml 2% cupferron solution is added and after standing 15 minutes the solution is extracted with 20 ml chloroform. This removes iron as cupferrate (and certain other metals). Generally three chloroform extracts will remove all the metal complexes and a further two extractions will remove excess cupferron.

The sodium hydroxide is prepared as a 10% solution. It is heated to boiling and 1 ml 2% magnesium chloride is added. After 10 minutes hot digestion the magnesium hydroxide with co-precipitated iron hydroxide is filtered off and the solution is then stored in a polythene container.

Using these purified reagents the blank was reduced to the equivalent of 0.0003% iron. In analysis of tungsten of low iron contents it would still be advisable to carry out a reagent blank.

Hydrofluoric/nitric acid mixture was used for solution of the tungsten. It was found that it was necessary to add citric acid before evaporating to dryness to remove hydrofluoric acid, otherwise some of the iron remained insoluble on treating with sodium hydroxide.

The final procedure is as follows;

Dissolve 1 g tungsten *(Note 1)* in 2 ml hydrofluoric acid and 1 ml nitric acid in a covered platinum dish. When the tungsten is completely dissolved rinse the lid with water and add 20 ml 10% citric acid solution (purified). Evaporate the solution to dryness on the water bath. (If a hot plate is used, care must be taken to avoid charring the citric acid). Add 10 ml 10% sodium hydroxide solution (purified) and warm the solution to dissolve the tungstic oxide. (The solution should be alkaline and if necessary a few more drops of sodium hydroxide solution should be added).

Now add 20 ml 10% citric acid solution (purified); this should give a solution of pH between 4 and 7. (This should be checked with indicator papers and adjusted if necessary, with sodium hydroxide or citric acid, to come within this range).

Transfer the solution to a separating funnel and add 20 ml 10% sodium dithionite solution (pre-extracted). Leave the solution to stand 15 minutes to complete the reduction of the ferric ion to ferrous iron, then add 20 ml of 0.05% 4,7-diphenyl-1,10-phenanthroline in alcoholic solution, (either absolute ethyl alcohol ANALAR, or an iron-free grade of industrial spirits, can be used). Add 10 ml chloroform and extract the red iron complex. Transfer the chloroform extract to a 50 ml graduated flask and repeat the extraction with a further 5 ml chloroform. Combine the extracts and dilute to 50 ml with alcohol. Measure the absorption of the solution on the Spekker absorptiometer, using Ilford Spectrum Green No. 604 filters, 1 cm cells *(Note 2)* and a 1.0 water/water setting.

Note I

This procedure covers the range 0 to 0.012% iron. If more iron is expected a smaller starting weight can be taken.

Note II

For iron contents in the range 0 to 0.003% a 4 cm cell can be used.

To prepare the calibration curve, a standard iron solution is required, Dissolve 0.1 g H.H.P. iron in 10 ml hydrochloric acid and 2 ml nitric acid, and evaporate the solution to dryness. Dissolve the residue in 2 ml hydrochloric acid and dilute to 100 ml. Dilute 5 ml of this solution to 500 ml with water. 1 ml of this solution contains 10 μg iron.

Take 0, 1, 2, 3, . . . 12 ml of the dilute standard iron solution. To each add 6 ml 10 % citric acid solution, followed by 2 ml 10% sodium hydroxide solution. This should give a solution in the correct pH range (4 to 7). Transfer each to a separating funnel, add 20 ml 10% sodium dithionite solution (pre-extracted) and proceed as before.

The recovery of iron was investigated, using this method. To two samples of 1 g tungsten, of previously determined iron content, 40 μg and 80 μg iron were added. 38 μg and 79 μg iron respectively were recovered. This was considered satisfactory at this level of iron impurity.

Table I gives the analysis of certain tungsten samples using this method. The second column are figures obtained by the General Electric Company Research Laboratories, using an (unpublished) polarographic method.

TABLE I

Tungsten sample	*% Iron found by absorptiometric method*	*% Iron found by G.E.C. polarographic method*
WZ19	0.010(1) %	0.009 %
BB73	0.004(8) %	0.004 %
VAC41	0.006(2) %	0.006 %
DZ187	0.005(2) %	0.005 %*
VCC28	0.015 %	0.014 %
X2	0.005(7) %	0.005 %

* Lead was present in this sample and this interfered with the polarographic method. This figure was obtained using a colorimetric method (thioglycollic acid).

Agreement between the two methods is very good.

Acknowledgement is due to Mr. L. J. DAVIES, Director of Research, The British Thomson-Houston Co. Ltd., Rugby, for permission to publish this paper.

SUMMARY

A method is proposed for the determination of iron present as an impurity in tungsten. 4,7-diphenyl-1,10-phenanthroline forms a stable complex with iron (present as the ferrous ion) which can be extracted by chloroform, in presence of alcohol, and determined absorptiometrically. Tungsten is complexed as citrate, and iron is reduced with sodium dithionite.

RÉSUMÉ

Une méthode est proposée pour le dosage du fer, présent comme impureté dans un tungstène. La 4,7-diphényl-1,10-phénanthroline forme avec le fer(II) un complexe stable pouvant être extrait par le chloroforme (en présence d'alcool) et dosé absorptiométriquement. Le tungstène est complexé comme citrate, et le fer est réduit par le dithionite de sodium.

ZUSAMMENFASSUNG

Es wird eine Methode vorgeschlagen, um Eisen zu bestimmen, welches sich als Verunreinigung in Wolfram befindet. Das 4,7-Diphenyl-1,10-phenanthrolin bildet mit dem Eisen(II) einen stabilen Komplex, welcher mit Chloroform (in Gegenwart von Alkohol) ausgezogen und absorptiometrisch bestimmt werden kann. Das Wolfram wird als Zitrat komplexiert, und das Eisen mit Natriumdithionit reduziert.

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* We stated in the text that the reagent was specific for iron. Subsequent work showed this to be incorrect. Cobalt, in presence of sodium dithionite, also gives an extractable brown coloured complex, although in absence of a strong reducing agent no such cobalt complex is formed. (It is possible that the reagent reacts with cobalt in a stabilized monovalency state).

Under the conditions given 1% cobalt = 0.018% iron, so that the effect of cobalt can normally be neglected.

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SÉPARATION DES TRACES DE BORE PAR EXTRACTION DU FLUOBORATE DE TÉTRAPHÉNYLARSONIUM

par

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Les deux principales méthodes de séparation des traces de bore sont l'utilisation d'une résine échangeuse d'ions[1] et la distillation de l'ester méthylborique[2].

Or, on sait[3] que la plupart des anions de formule générale AB_4^- donnent avec les cations tétraphénylphosphonium, — arsonium et — stibonium des composés peu solubles dans l'eau, mais solubles dans le chloroforme. Nous avons pensé qu'il serait possible, en extrayant le fluoborate de tétraphénylarsonium, de séparer les traces de bore contenues dans une solution aqueuse.

Le bore est ensuite dosé par la méthode de PHILIPSON[4]: on forme un composé coloré obtenu entre l'acide borique et la curcumine. L'intensité de la coloration dépendant de la quantité de bore, cette dernière est déterminée par spectrophotométrie.

I. ÉTUDE THÉORIQUE DES ÉQUILIBRES

La séparation comporte deux stades: transformation de l'acide borique en fluoborate et extraction du fluoborate de tétraphénylarsonium.

(1) *Formation de l'ion fluoborique*

En milieu acide (pH < 7), tout le bore est sous forme d'acide borique, le pK de ce dernier étant égal à 9.2.

Pour un pH inférieur au pK de l'acide fluorhydrique, le fluorure en solution est principalement sous forme d'acide fluorhydrique et on peut écrire l'équilibre:

$$HBO_2 + 4\,HF \rightleftarrows BF_4^- + H^+ + 2\,H_2O \qquad (1)$$

Pour un pH supérieur au pK, l'acide est totalement ionisé et l'équilibre précédent s'écrira:

$$HBO_2 + 4\,F^- + 3\,H^+ \rightleftarrows BF_4^- + 2\,H_2O \qquad (2)$$

Donc pour un pH $<$ pK il faut se placer en milieu le moins acide possible et pour pH > p*K* en milieu le plus acide possible pour déplacer l'équilibre vers la formation de BF_4^-. Le pH optimum est donc 3.2, p*K* de l'acide fluorhydrique.

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Mais à l'équilibre précédent se superpose celui correspondant à l'hydrolyse du fluoborate:

$$BF_4^- + H_2O \rightleftarrows BF_3OH^- + H^+ + F^- \tag{3}$$

qu'il faut déplacer vers la gauche, c'est-à-dire diminuer le pH.

De plus, l'équilibre (1) ou (2) est déplacé vers la droite lorsqu'on augmente la concentration totale en fluorure. Par contre, l'équilibre (3) est déplacé vers la gauche. On a donc intérêt à augmenter la concentration totale en fluorure.

Ces résultats qualitatifs peuvent être précisés quantitativement:

Aux deux équilibres précédents correspondent les deux lois d'action de masses:

$$\frac{[BF_4^-]}{[HBO_2]\,[F^-]^4\,[H^+]^3} = K_1 \tag{4}$$

$$\text{et}\quad \frac{[BF_3OH^-]\,[H^+]\,[F^-]}{[BF_4^-]} = K_2 \tag{5}$$

auxquelles s'ajoute celle relative à la dissociation de l'acide fluorhydrique:

$$\frac{[H^+]\,[F^-]}{[HF]} = K_A \tag{6}$$

De plus, on peut écrire les bilans du bore et du fluor:

$$C_0 = [HBO_2] + [BF_4^-] + [BF_3OH^-] \tag{7}$$

$$C_1 = [HF] + [F^-] + 3\,[BF_3OH^-] + 4\,[BF_4^-] \tag{8}$$

en appelant C_0 et C_1 les concentrations totales en bore et en fluorure. Or, dans les conditions pratiques d'utilisation, la concentration totale maximum du bore est $2 \cdot 10^{-5} M$ et la concentration totale minimum du fluor $10^{-2} M$. On peut donc négliger les concentrations du fluoborate et de l'ion BF_3OH^- devant celles de F^- et de HF dans le bilan du fluor. En éliminant [HF], $[F^-]$, $[BF_3OH^-]$ et $[HBO_2]$ entre les 5 équations précédentes, il vient:

$$\frac{[BF_4^-]}{C_0} = \frac{1}{1 + \dfrac{\left(1 + \dfrac{[H^+]}{K_A}\right)^4}{K_1\,C_1^4[H^+]^3} + \dfrac{K_2}{C_1[H^+]}\left(1 + \dfrac{[H^+]}{K_A}\right)} \tag{9}$$

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Les 2ème et 3ème termes du dénominateur correspondent respectivement aux équilibres (2) et (3). A l'aide de cette relation, on peut retrouver les résultats qualitatifs précédemment établis, tant en ce qui concerne l'action du pH que celle de la concentration totale en fluorure.

L'activité du corps dépend de la force ionique qui doit, en principe, être maintenue constante au cours des mesures.

En outre, les équilibres précédents s'établissent lentement et il y a lieu de déterminer expérimentalement le temps nécessaire aux réactifs pour atteindre un état d'équilibre ou, tout au moins, pour que l'on n'observe plus de variation des concentrations au cours du temps.

(2) *Extraction du fluoborate de tétraphénylarsonium*

Le réactif utilisé est le chlorure de tétraphénylarsonium qui est soluble dans l'eau et le chloroforme. On a l'équilibre:

$$\underset{\text{chloroforme}}{As(C_6H_5)_4Cl} \rightleftarrows \underset{\text{eau}}{As(C_6H_5)_4^+} + Cl^- \qquad (10)$$

Avec le fluoborate on peut écrire:

$$\underset{\text{chloroforme}}{As(C_6H_5)_4BF_4} \rightleftarrows \underset{\text{eau}}{As(C_6H_5)_4^+} + BF_4^- \qquad (11)$$

L'extraction du fluoborate est favorisée lorsque la concentration du réactif augmente. Si elle n'est pas quantitative, il faut effectuer plusieurs extractions successives de la solution aqueuse. Enfin, on doit déterminer le temps de contact minimum entre les deux phases au-delà duquel les concentrations ne varient plus.

La loi d'action de masses relative à l'équilibre (11) est:

$$\frac{[As(C_6H_5)_4BF_4]_{CHCl_3}}{[As(C_6H_5)_4^+]_{aq.}\ [BF_4^-]_{aq.}} = K \qquad (12)$$

Si C_2 est la concentration initiale du fluoborate dans la phase aqueuse, le bilan du bore s'écrit, en supposant que les volumes des deux phases sont égaux:

$$C_2 = [BF_4^-]_{aq.} + [As(C_6H_5)_4BF_4]_{CHCl_3} \qquad (13)$$

En éliminant $[BF_4^-]$ entre les relations (12) et (13) il vient:

$$\frac{\dfrac{[As(C_6H_5)_4BF_4]_{CHCl_3}}{C_2}}{1 - \dfrac{[As(C_6H_5)_4BF_4]_{CHCl_3}}{C_2}} = K[As(C_6H_5)_4^+]_{aq.} \qquad (14)$$

La concentration totale du chlorure de tétraphénylarsonium est de l'ordre de $10^{-2}M$. Sa variation au cours de la réaction est négligeable. On peut donc considérer $[\mathrm{As(C_6H_5)_4}^+]_{aq}$. comme étant également constante. Dans ces conditions, on voit d'après l'équation (14) que même si l'extraction n'est pas quantitative, le rapport entre la quantité de bore extraite et la quantité initiale de fluoborate est indépendante de cette dernière.

II. RESULTATS EXPERIMENTAUX

1) *Conditions opératoires et dosage du bore*

Les essais sont effectués de la façon suivante: à 4 ml de mélange tampon HF/F^- ou d'acide fluorhydrique est ajouté 1 ml d'une solution aqueuse contenant 1 p.p.m. de bore ou 1 ml d'eau distillée pour les essais à blanc.

La solution obtenue est extraite par 5 ml d'une solution chloroformique de chlorure de tétraphénylarsonium. Le bore est dosé dans le solvant par la méthode de PHILIPSON[4].

Nous avons observé, qu'après séchage à l'étuve, le résidu ne se redissout pas toujours totalement dans l'alcool et les résultats obtenus sont aberrants. Ceci est dû au chlorure de tétraphénylarsonium présent dans le chloroforme. En effet, nous avons constaté que le trichloracétate de tétraphénylarsonium est peu soluble dans l'eau mais assez soluble dans l'alcool. Or, après avoir amené à sec en présence d'hydroxyde de sodium, on ajoute 1 ml d'acide trichloracétique et 1 ml de curcumine en solution dans l'alcool. Cette quantité est insuffisante pour redissoudre le sel formé et il faut rajouter 1 ml d'alcool. Dans ces conditions, les résultats sont corrects et reproductibles. Le mode opératoire exact et les concentrations des différents réactifs sont indiqués page 385.

Nous avons préparé une solution contenant 1 p.p.m. de bore par dilution d'une solution à 200 p.p.m. obtenue par pesée et dissolution d'un poids connu de borax R.P. La verrerie jaugée est inutilisable pour prélever avec précision des volumes de mélanges tampons HF/F^-. Ces volumes sont déterminés par pesée des solutions de densité connue. Celle-ci est déterminée par pesée d'un volume connu mesuré à la pipette pour les solutions de concentration inférieure à $2M$. Pour les solutions d'acide concentré, elle est obtenue en appliquant la règle des mélanges sachant que l'acide fluorhydrique à 40% a une densité égale à 1.13.

Tous les essais sont effectués dans des récipients en polyéthylène.

Les densités optiques D sont déterminées par rapport à l'alcool au moyen d'un spectrophotomètre Jean-Constant. Pour 1 μg de bore on obtient $D = 0.62$ et pour 0 μg, $D = 0.09$. Ces déterminations ne sont pas faites sur une solution de borax mais dans les conditions utilisées: à 5 ml d'une solution chloroformique de chlorure de tétraphénylarsonium on ajoute 1 ml d'une solution à 1 p.p.m. de bore ou 1 ml d'eau distillée et effectue le dosage sur ce mélange.

2) *Formation de l'ion BF_4^-*

Temps nécessaire pour atteindre l'équilibre. La solution aqueuse (bifluorure d'ammonium $0.8M$ ou acide fluorhydrique-fluorure de sodium respectivement $0.4M$, 0 ou 1 μg de bore) est abandonnée un certain temps puis extraite par du chloroforme (chlorure de tétraphénylarsonium $10^{-2}M$) en agitant mécaniquement pendant 1 heure.

Les résultats sont indiqués sur les courbes représentées Fig. 1. On voit qu'après un délai de 18 heures, les concentrations ne varient plus.

Influence du pH. Les essais sont effectués comme précédemment, avec un temps de contact égal au moins à 18 heures.

Le pH ne pouvant être déterminé à l'aide d'une électrode de verre, il est calculé en supposant le pK de l'acide fluorhydrique égal à 3.2 et en faisant varier d'une façon connue le rapport $[HF]/[NaF]$. La concentration totale du fluorure ($[HF] + [NaF]$)

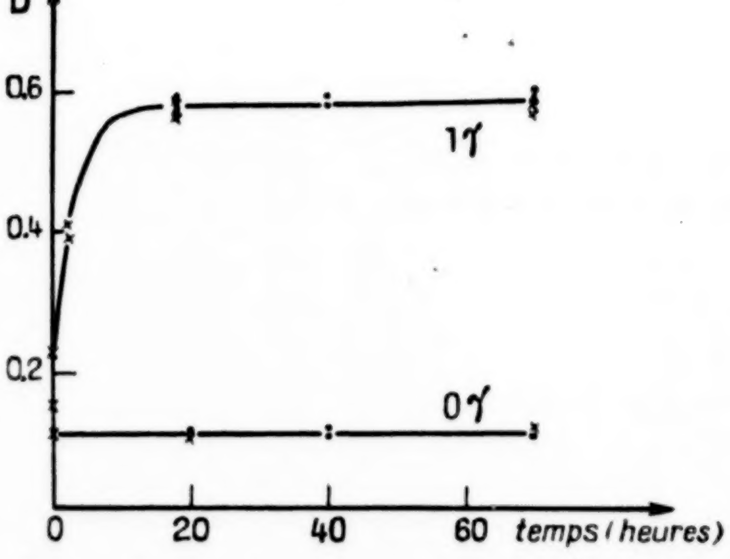

Fig. 1. Temps nécessaire pour atteindre l'équilibre
. Mélange tampon HF/NaF
x Mélange tampon HF/NH_4F

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est maintenue constante et égale à 0.16M (courbe 1, Fig. 2) et 0.8M (courbe 2, Fig. 2). Il n'est pas tenu compte des variations de force ionique.

Vers les milieux acides, on n'observe pas de diminution de la concentration de l'ion BF_4^- à l'encontre des prévisions théoriques. Ceci peut être interprété par le fait que la diminution du 2ème terme du dénominateur de l'équation (9) est négligeable devant l'augmentation du 3ème terme aux pH considérés, et qu'elle serait notable à des pH plus faibles. Ceci semble être confirmé par les résultats obtenus lorsqu'on opère à différentes concentrations d'acide fluorhydrique seul: bien que la concentration totale en fluorure augmente, on observe une diminution de la concentration en fluoborate (Fig. 3).

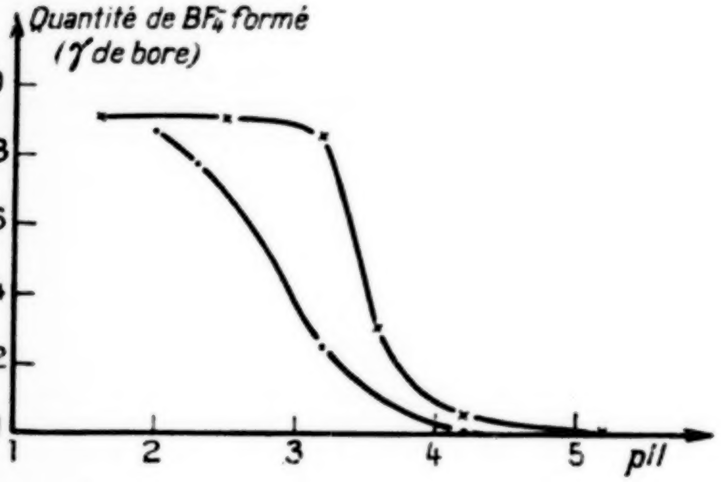

Fig. 2. Formation de BF_4^- en fonction du pH
x concentration totale du fluorure 0.8M
. concentration totale du fluorure 0.16M.

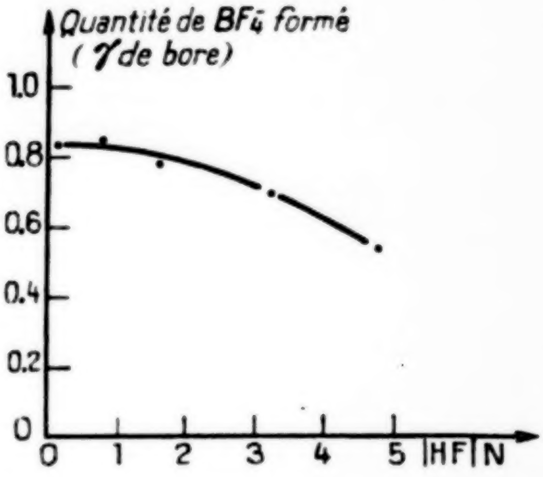

Fig. 3. Formation de BF_4^- en fonction de la concentration de HF.

Influence de la concentration totale du fluorure. Les essais sont effectués comme précédemment. Le pH est maintenu constant, aux variations de force ionique près, et égal à 3.2 en utilisant un rapport [HF]/[NaF] ou [HF]/[NH_4F] constant et égal à 1. Les résultats sont indiqués Fig. 4.

3) *Extraction du fluoborate de tétraphénylarsonium*

Temps nécessaire pour atteindre l'équilibre entre les 2 phases. Les essais sont effectués avec un mélange tampon tel que [HF] = [NaF] = 0.4M. Les deux phases sont agitées mécaniquement pendant un temps variable. Les résultats sont indiqués Fig. 5. Il faut donc agiter pendant au moins 30 minutes pour atteindre l'équilibre.

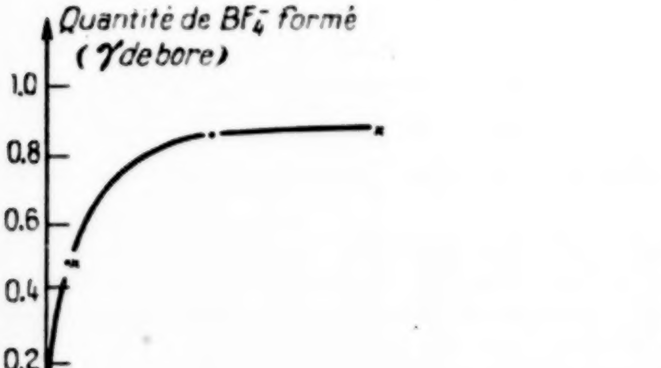

Fig. 4. Influence de la concentration totale du fluorure sur la formation de BF_4^-

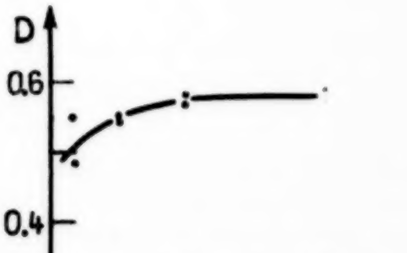

Fig. 5.

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Influence de la concentration du chlorure de tétraphénylarsonium. Les conditions expérimentales sont analogues aux précédentes. Le chlorure de tétraphénylarsonium est dissout en quantités variables dans le chloroforme. On voit sur la Fig. 6 qu'il semble y avoir un maximum pour une concentration égale à $10^{-2}M$. Ceci peut être interprété par le fait qu'une trop grande quantité de réactif perturbe le dosage colorimétrique.

Influence du nombre d'extractions. En aucun cas nous n'avons retrouvé plus de 90% du bore initialement introduit dans la solution. Nous avons essayé d'effectuer plusieurs extractions successives de la phase aqueuse, les différentes solutions chloroformiques étant ensuite rassemblées. Les résultats sont indiqués dans le Tableau I.

TABLEAU I

Composition de la solution aqueuse	*Nombre d'extractions*	*Densité optique (0γ)*	*Densité optique (1γ)*	*% de bore trouvé*
[HF] = $0.4M$	1	0.11-0.12	0.56-0.59	87
[NaF] = $0.4M$	2	0.11-0.13	0.58-0.59	87
	4	0.13-0.15	0.56-0.56	79
Bifluorure	1	0.12-0.14	0.56-0.59	84
d'ammonium	2	0.10-0.11	0.59-0.60	93
$0.8M$	4	0.14-0.15	0.56-0.59	81

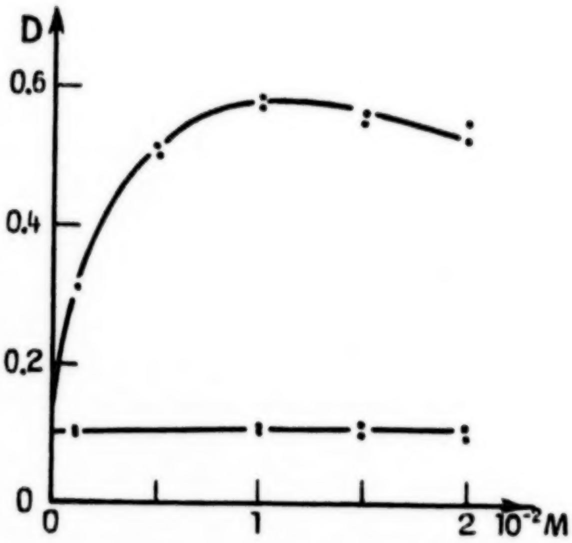

Fig. 6. Influence de la concentration du chlorure de tétraphénylarsonium sur l'extraction du fluoborate.

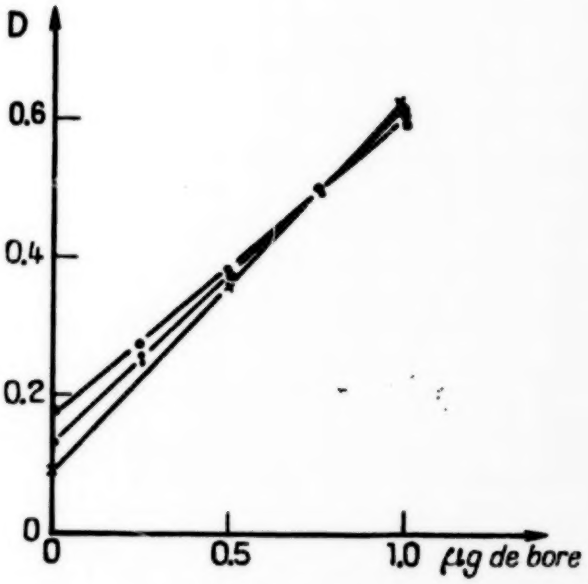

Fig. 7. Courbes d'étalonnage
x sans fluorure
. acide fluorhydrique $0.8N$
o acide fluorhydrique $2.4M$
fluorure de sodium $0.08M$

Il semble que plusieurs extractions successives n'augmentent pas la quantité de bore retrouvée et qu'au contraire on observe une diminution du rendement de l'extraction. Cette anomalie provient vraisemblablement du fait que la quantité de chlorure de tétraphénylarsonium augmente avec le nombre d'extractions et perturbe le dosage final.

Comme nous l'avons fait remarquer page 382, même si l'extraction n'est pas quantitative, il est possible d'effectuer le dosage. On perd en sensibilité, car pour un essai à blanc donné, la variation de densité optique de la solution contenant 1 γ de bore est inférieure à 0.53. En se plaçant dans des conditions où l'extraction est suffisamment quantitative (80 à 90% par exemple), la sensibilité est peu diminuée. Comparer les courbes représentées Fig. 7. On voit que la loi de Beer est suivie dans tous les cas.

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4) *Mode opératoire*

Nous proposons le mode opératoire suivant pour la séparation et le dosage de quantités de bore comprises entre 0.05 et 1 μg dans 5 ml de solution.

5 ml de solution aqueuse de pH inférieur à 3.2 et contenant une concentration totale de fluorure au moins égale à 0.8*M* sont abandonnées pendant au moins 18 heures. Ajouter alors 5 ml d'une solution chloroformique de chlorure de tétraphénylarsonium et agiter mécaniquement pendant 30 minutes. Le mélange est centrifugé. Retirer la solution aqueuse avec une pipette en polyéthylène, ajouter 5 ml d'eau distillée puis retirer. Ajouter à nouveau 5 ml d'eau distillée et agiter quelques instants, centrifuger et retirer la phase aqueuse. Cette dernière opération est effectuée deux fois. La solution chloroformique est mise dans une capsule de platine. Le tube en polyéthylène où a été effectuée l'extraction est rincé par 1 ml de chloroforme que l'on ajoute à la solution précédente. Dans la capsule de platine mettre 15 gouttes d'hydroxyde de sodium 0.1*N*, et une goutte de phénolphtaléine, amener à sec en plaçant la capsule sous une rampe chauffante constituée par un tube de silice de 40 cm de long à l'intérieur duquel est placé une résistance chauffante (puissance consommée: environ 900 W).

Le résidu solide est repris par 1 ml d'acide trichloracétique *N*. Attendre 10 minutes. Ajouter 1 ml d'alcool à 95%, mélanger et dissoudre, puis ajouter 1 ml de curcumine. Mettre à l'étuve à 106 ± 1° C pendant 60 ± 3 minutes. Reprendre le résidu par l'alcool, amener à 25 ml et effectuer la colorimétrie dans une cuve de 1 cm à 5400 A.

Réactifs. La solution de chlorure de tétraphénylarsonium $10^{-2}M$ obtenue par dissolution de 1.046 g du sel cristallisé dans 250 ml de chloroforme R.P.
Solution de phénolphtaléine, à 0.1% dans l'alcool.
Solution de curcumine à 0.125% par dissolution du produit solide dans l'alcool.

Remarques. Lorsqu'on change un réactif, en particulier les mélanges tampon, il faut nécessairement effectuer un essai à blanc dans des conditions identiques à celles du dosage.

Ne pas conserver la solution de curcumine plus d'un mois.

Le chloroforme utilisé contient 0.5% d'alcool. Il est inutile de le laver à l'eau avant les extractions. L'alcool est retiré au cours des différents lavages et il n'y a pas de risque de volatilisation de borate d'éthyle lorsqu'on amène à sec.

L'eau distillée peut contenir du bore. Nous n'avons pas eu à purifier l'eau utilisée qui contenait de 3 à 4 μg de bore par litre.

La température n'étant pas uniforme dans l'étuve, les capsules abandonnées dans les parties froides donnent des résultats systématiquement trop faibles. Il faut donc déterminer, avec une solution de borax par exemple, les régions utilisables.

Après extraction, deux lavages sont effectués pour éliminer les produits contenus dans les dernières traces de solution aqueuse qu'on ne peut enlever à la pipette. Il est possible, comme cela a déjà été fait pour l'extraction du perrhénate[5], de sécher le chloroforme avec 1 à 2 g de sulfate de sodium anhydre, au lieu d'effectuer les lavages. Les résultats obtenus sont identiques, mais plus dispersés. En effet, après séchage à l'étuve, au lieu d'obtenir de fines aiguilles de trichloracétate de sodium, on obtient une laque difficile à sécher et souvent carbonisée. Elle est due au trichloracétate de tétraphénylarsonium, ce cation n'étant pas, en majeure partie, éliminé du chloroforme, comme précédemment.

5) *Contrôle de la méthode*

Afin de contrôler la méthode, nous avons effectué un certain nombre de déterminations sur des solutions aqueuses de compositions différentes. Les courbes d'étalonnage correspondantes sont représentées Fig. 7. Les résultats obtenus sont groupés dans le Tableau II.

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TABLEAU II

Composition de la solution aqueuse.	*Densité optique lue*	*Quantité de bore (γ)* *mise*	*trouvée*
[HF] = 2.4*N* [NaF] = 0.08*M*	0.180-0.185	0.00	0.00-0.04
	0.230-0.225	0.12	0.13-0.12
	0.270-0.275	0.19	0.12-0.22
	0.210-0.225	0.08	0.08-0.11
	0.240-0.250	0.14	0.15-0.17
	0.210-0.215	0.10	0.08-0.09
[HF] = 0.8*N*	0.150-0.150	0.08	0.05-0.05
	0.130-0.135	0.00	0.00-0.01
	0.190-0.195	0.14	0.12-0.14
	0.140-0.155	0.06	0.03-0.05
	0.130-0.130	0.03	0.00-0.00
	0.210-0.217	0.20	0.20-0.21
	0.250-0.315	0.40	0.28-0.40
	0.240-0.280	0.30	0.26-0.34
	0.155-0.175	0.10	0.09-0.13

6) Précision de la méthode

Nous avons observé que quelle que soit la quantité de bore, l'erreur absolue maximum sur une détermination est constante et égale à 0.015 unité de densité optique ce qui correspond à environ 0.03 ou 0.04 γ de bore. Cet écart est en accord avec les résultats obtenus (Tableau II). En séchant sur du sulfate de sodium, l'erreur est de 0.025 à 0.03 unité de densité optique.

Parfois, on obtient un résultat beaucoup trop faible dû à une redissolution incomplète du trichloracétate de tétraphénylarsonium par l'alcool.

Nous remercions Mme M. Buvet et M. C. Cornet pour leur collaboration et pour les suggestions qui permirent de mener à bien ce travail.

RÉSUMÉ

On décrit une méthode de séparation des traces de bore par extraction du fluoborate de tétraphénylarsonium par le chloroforme. Le dosage du bore est ensuite effectué par la méthode de Philipson.

SUMMARY

A description is given of the method of separating traces of boron by extraction from tetraphenylarsonium - fluoroborate, using chloroform. The determination of boron is then carried out by the Philipson method.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben, um Spuren von Bor durch eine Extraktion von Tetraphenylarsoniumfluoborat mit Chloroform abzutrennen. Die Bestimmung von Bor wird darauf nach der Methode von Philipson ausgeführt.

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USE OF A REFLECTANCE ATTACHMENT TO OBTAIN EXCITATION SPECTRA

by

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A plot of the intensity of fluorescence versus the wavelength of the exciting radiation produces an excitation spectrum which, for a particular combination of source and receiver, is characteristic of a substance over a limited range of concentrations[1]. The chief reason for studying excitation spectra is to determine the wavelength of exciting radiation which will produce the maximum difference in reading due to production of fluorescence. Unfortunately, 365 mμ and 436 mμ, which are most often employed in fluorimeters, may be comparatively inefficient for exciting fluorescence. By obtaining an empirical excitation spectrum and then using for excitation the wavelength at the maximum, one can sometimes improve the sensitivity of a fluorimetric determination even though the intensity of the source may be less at that wavelength than at 365 mμ or 436 mμ.

It has long been recognized that the best arrangement for the measurement of fluorescence is one in which the source and the receiver are close together and facing the same side of the cell containing the fluorescing sample. Such an arrangement is found in the reflectance attachment for the Beckman DU spectrophotometer. In order to minimize the need for secondary filters, samples were backed by a highly absorbent material, ,,soft" glass for the ultraviolet and black glass or black cloth for the visible spectrum. The resulting level of light, even for a strongly fluorescing solution, was usually very low when compared with the reflectance from a white material such as magnesium carbonate, and hence the desirability of comparison, not against a white standard, but against a comparable black blank. In the present study some measurements were also made against another solution containing a different concentration of the same fluorophor. Use of the differential method facilitated the detection of nonlinear responses arising from self-absorption and other factors.

Aqueous alkaline solutions of dichlorofluorescein (DCF) were employed for most of the experiments. Qualitative effects of introducing a quenching agent and of introducing another solvent are reported to illustrate the results of differential runs.

EXPERIMENTAL DETAILS

Reagents and Solutions

Portions from a stock solution containing 0.1045 g per liter of "indicator grade" of dichlorofluorescein (Eastman Kodak Co.) in a 0.1*M* sodium carbonate were used from time to time to prepare more dilute standards containing between 10^{-5} and 10^{-2}% by weight. In every case, 0.1*M* sodium carbonate was used to make the dilution.

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Brief studies were also made with several other derivatives of fluorescein, all of which were employed, without further purification in the most nearly pure from supplied by Eastman Kodak Company.

Equipment

Though some measurements were made on a continuous-recording spectrophotometer designed and built by Professor A. C. HARDY, most of the measurements were obtained using a Beckman Model DU Spectrophotometer fitted with standard reflectance and photomultiplier attachments. Because the sample holder supplied with reflectance attachment could hold only one sample in addition to the standard, another holder having roughly the same external dimensions was constructed from aluminum and fitted with three brass cover plater 25 mm wide. A hole 12 mm in diameter was cut in each plate to expose the sample below. This permitted a blank and a standard to be read along with each sample. The usual light field from the monochromator was restricted by substituting, for the larger aperture located just above the sample compartment, an aluminum ring (painted black) 5 mm thick with an opening 12 mm in diameter. Cells of 35 mm in diameter were made from pyrex tubing by fusing a short section to a flat pyrex disc and grinding the walls of the tube until the cell had a depth of 1.00 mm. Quartz cover glasses were employed.

Procedures

Before being used, each cell was carefully washed with distilled water and dried. A sample was then poured into a cell until an inverted meniscus was formed. A uniform sample depth was insured by sliding a quartz cover slip over the top in such a way as to exclude air bubbles. A filled cell was mounted in the reflectance attachment over polished black glass. Against magnesium carbonate, the reflectance of the glass was about 1% (black cloth is about 3%) so most of the incident radiation which passed through the sample was absorbed and hence prevented, without the use of a filter, from reflecting into the photocell compartment along with the desired fluorescence radiation. To minimize variations arising from differences between cells, one particular cell was always used for the standard and another for the sample.

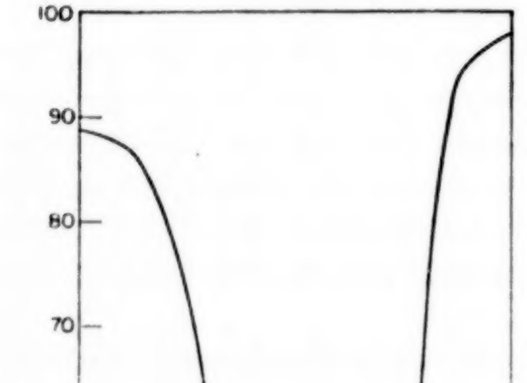

Fig. 1. Absorption spectrum for 0.001% dichlorofluorescein in 0.1*M* sodium carbonate (not corrected for fluorescence).

For highest sensitivity, a sample was compared against a blank of 0.1*M* sodium carbonate mounted on a similar black background. The slit and or the sensitivity of the instrument was increased until the arbitrary reflectance value of the blank was close to the maximum permitted by the instrument and preferably a simple multiple of its reflectance value against magnesium carbonate.

Differential measurements for comparing two samples, each containing the fluorophor, were made by selecting a constant arbitrary value for the standard at all wavelengths.

Readings were usually made on the "0.1" scale. As a result of the very low level of light, it was advantageous to minimize stray light from external sources by covering the photomultiplier and reflectance attachments with a double thickness of black cloth about 3 feet square.

RESULTS

A conventional absorption spectrum for DCF, uncorrected for fluorescence, is shown in Fig. 1. Note that the maximum absorbance occurs near 500 mμ. Essentially the same spectrum resulted when the solution was measured in the reflectance apparatus using white backing (magnesium carbonate), for both the sample and the blank. However, when the same cell and its blank were mounted over black glass, an excitation curve having a peak at 500-510 mμ was obtained (Fig. 2).

When a series of DCF solutions covering a wide concentration range was examined against magnesium carbonate, the curves for the more dilute solutions showed only small differences (curves 1 and 2 in Fig. 2). The difference can be magnified by working at a higher instrument sensitivity by virtue of using standards darker than magnesium carbonate, such as a mixture of magnesium carbonate and cupric oxide or simply black glass. Though it is also possible to realize a modest gain in sensitivity by working with deeper cells, self-absorption becomes more important (Fig. 3).

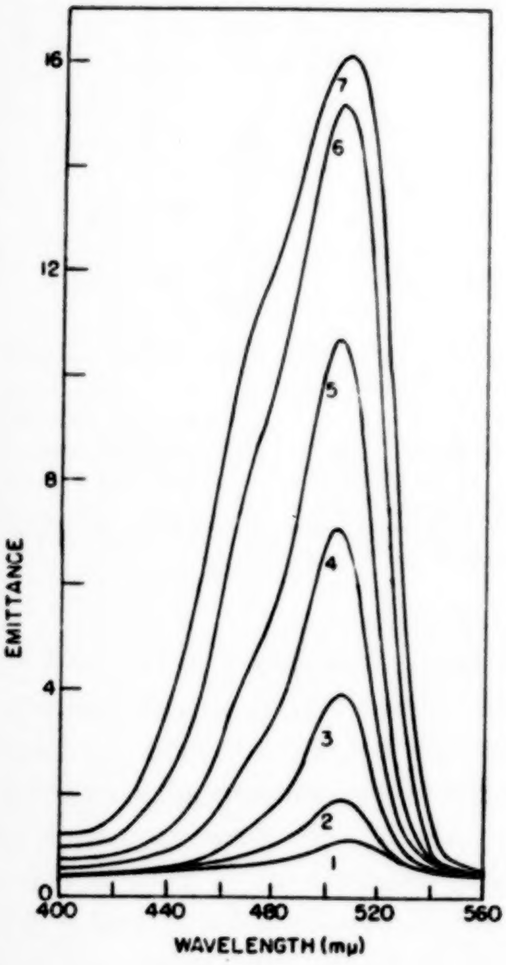

Fig. 2

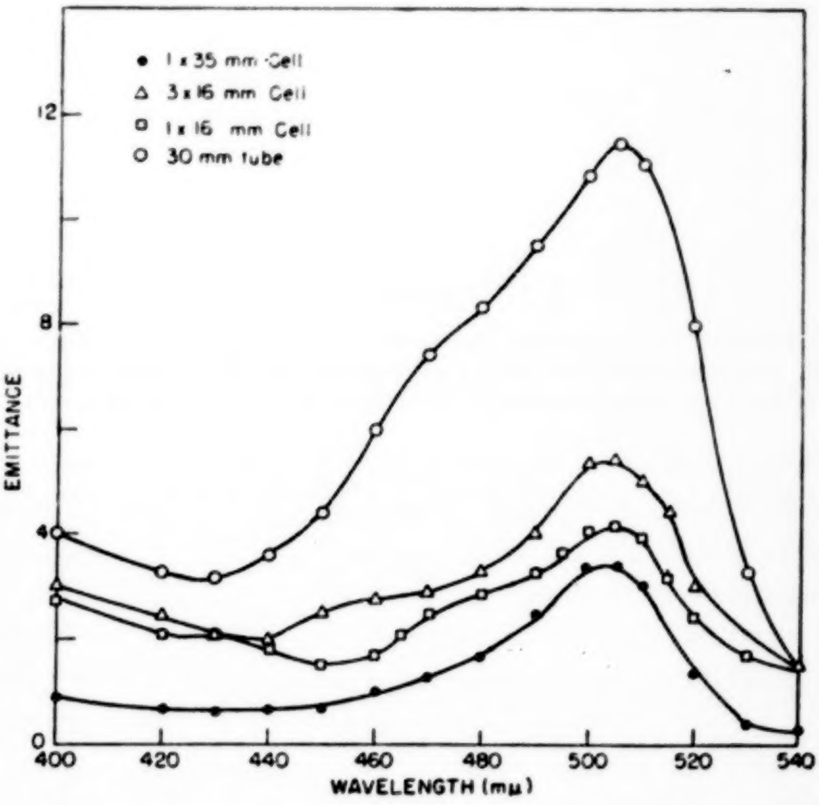

Fig. 3

Fig. 2. Excitation spectra of dichlorofluorescein in 0.1 M sodium carbonate obtained on the Hardy Spectrophotometer, using 1 × 35 mm cells.
Standard: 0.1 M sodium carbonate backed with magnesium oxide at 100.
Samples: (1) 0.0001%, (2) 0.0002%, (3) 0.0005%, (4) 0.001%,
(5) 0.002%, (6) 0.005%, (7) 0.010% DFC backed with black glass.
Fig. 3. Emittance of 0.0005% dichlorofluorescein in four types of cells compared to magnesium carbonate at 100.

From the standpoint of using these measurements for determining the concentration of DCF, the typical data in Fig. 4 demonstrate that such a goal is entirely feasible. In addition, it was interesting to find that despite the lower intensity of the tungsten source and the inefficient collection of the fluorescence by the reflectance attachment, the lowest detectable concentration of DCF in the 1 mm cell was essentially the same as that obtained with the Coleman photofluorometer, which is equipped with a mercury lamp (A-H_4) and holds the sample in a 16 mm diameter test tube. Therefore, it would appear possible to improve many fluorimetric analyses by using information from excitation spectra which in turn are closely related to absorption spectra.

The use of a standard consisting of another concentration of the same fluorophor mounted over black glass provides a ready means of obtaining standards with reflectance values between those of magnesium carbonate and of black glass alone (Fig. 5).

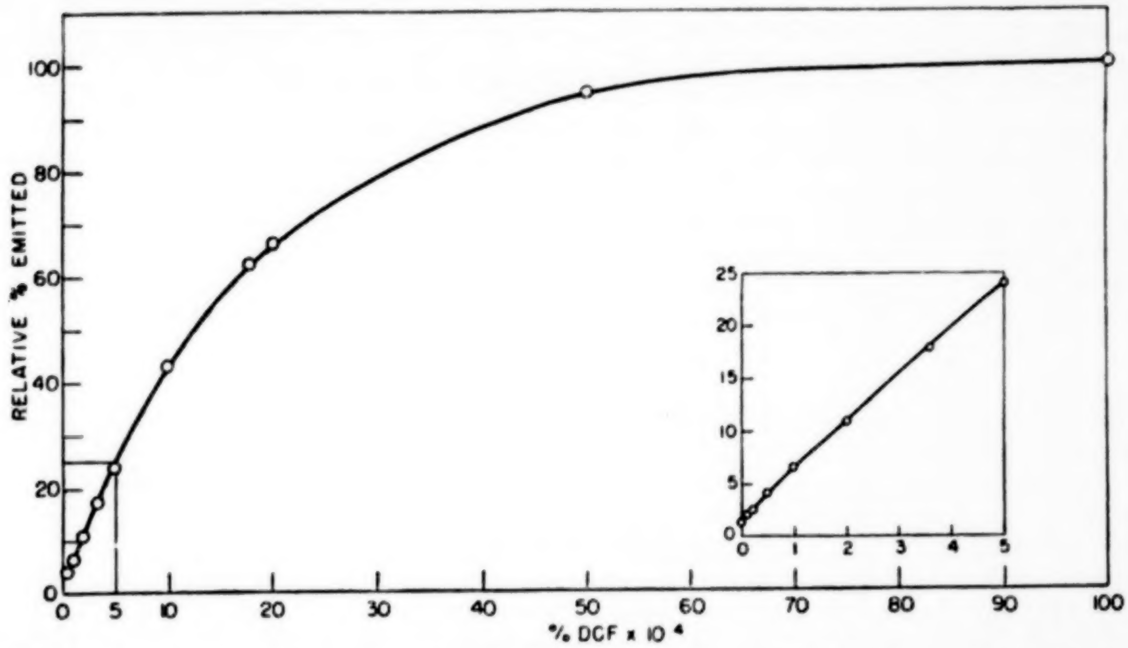

Fig. 4. Relationship between concentration of dichlorofluorescein and emittance at 505 mμ compared to a 0.01% solution of dichlorofluorescein (1 × 35 mm cells backed by black glass).

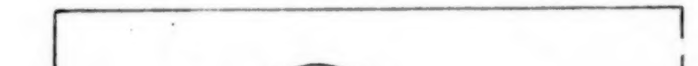

Fig. 5. Differential curves obtained using 30 mm tubes and 0.0003% dichlorofluorescein as a standardat 50. (1) $2 \cdot 10^{-5}$; (2) $5 \cdot 10^{-5}$; (3) $1 \cdot 10^{-4}$; (4) $2 \cdot 10^{-4}$; (5) $3 \cdot 10^{-4}$; (6) $5 \cdot 10^{-4}$%.

Though such standards can be used to facilitate quantitative measurements, the chief advantage afforded by such differential measurements appears to be in the study of self-absorption and of quenching phenomena. A typical comparison is shown in Figs. 6 and 7 for solutions of DCF containing sodium thiosulfate.

Preliminary experiments of the same type as those reported for DCF have been made with fluorescein and the dibromo-, tetrabromo-, diiodo-, and the tetraiodo-derivatives. From the typical curves shown in Fig. 8, one could predict that by making measurements at about 520 mμ it should be possible to detect and determine small amounts of DCF in fluorescein. By differential measurements one can handle the much less favorable case and detect unambiguously $1.6 \cdot 10^{-4}$% fluorescein in $1.8 \cdot 10^{-3}$% DCF by using $2.0 \cdot 10^{-3}\%$ DCF as a standard and measuring in the region 450-500 mμ.

DISCUSSION

It is readily apparent that the excitation spectrum will be a function of the intensity of the source at different wavelengths. Hence, a standardized source must be employed if one wishes to convert the results to fundamental values. Likewise the receiver should be calibrated using a standard source.

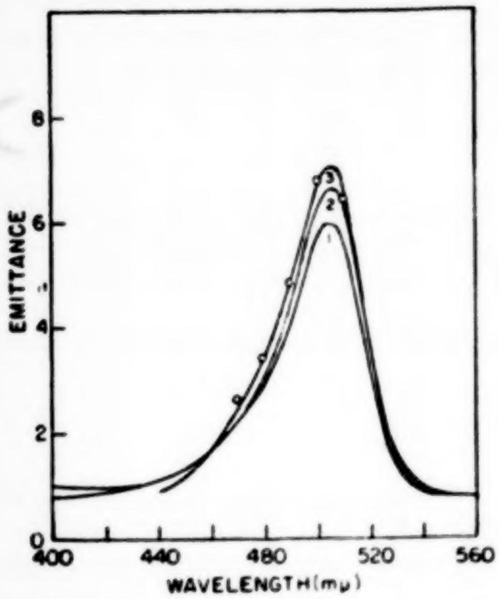

Fig. 6. Effect of thiosulfate on the excitation of 0.001% dichlorofluorescein recorded on the Hardy Spectrophotometer using 0.1 *M* sodium carbonate backed by magnesium oxide as 100. (1) 0.1 *M*; (2) 0.02 *M*; (3) 0.0 *M* thiosulfate backed by black glass.

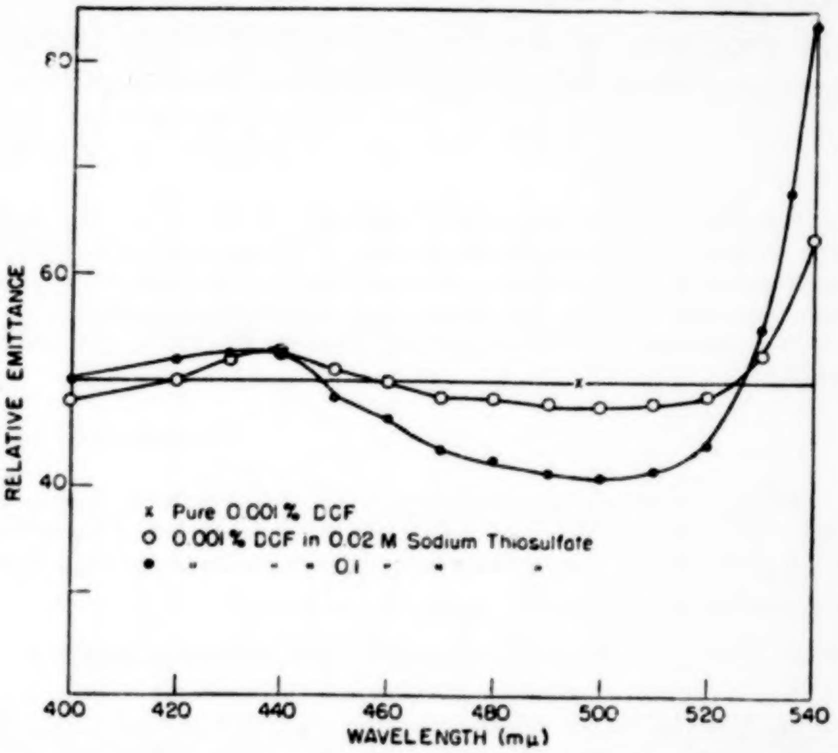

Fig. 7. Differential measurement of the effect of thiosulfate on the emittance using 0.001% dichlorofluorescein as a Standard at 50.

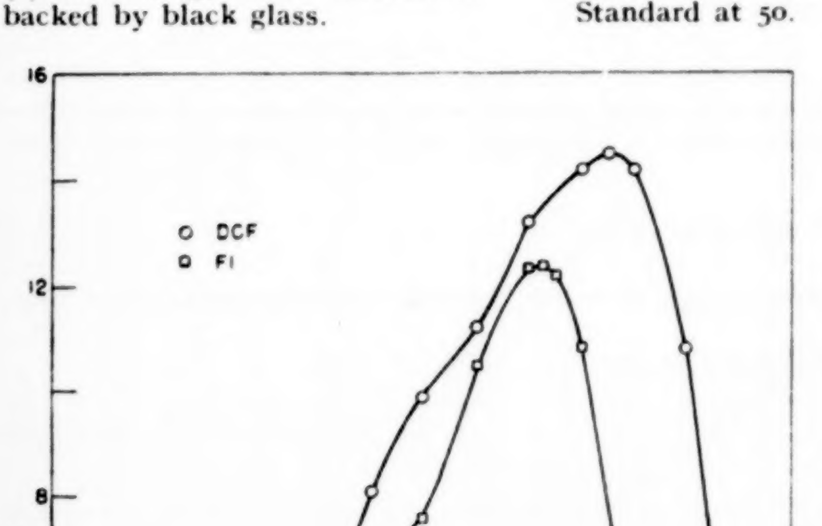

Fig. 8. Emittances of 0.01% dichlorofluorescein and 0.008% fluorescein compared to magnesium carbonate at 100.

The absorption curves of fluorescent compounds, when obtained in the usual way, will always be distorted by the fluorescence. Likewise, the emittance curves will be distorted by an overlapping absorption spectrum. Under the conditions of the present study, these interferences precluded precise comparisons of absorption and excitation maxima. In addition, the absence of a filter to remove scattered radiation of the exciting wavelength undoubtedly introduced other differences, particularly near the lower limit of detectable fluorescence. An extreme case was once encountered (zinc "oxinate" in chloroform) in which the fluorescing solution produced smaller readings in part of the spectrum than its corresponding blank. This was attributed to a combination of less scattered light from the sample, due to the presence of an absorbing compound, and the production of wavelengths of fluorescence radiation to which the receiver was less sensitive than those of the exciting wavelength[2].

ACKNOWLEDGEMENTS

The authors are very much indebted to Mr. A. G. HALL for construction of the cells and to Mr. R. H. GUSTAVSON for construction of the special cell compartment. The authors are also indebted to Professor A. C. HARDY for making his instrument available for measurements from which the performance of the Beckman instrument was evaluated.

The authors wish to thank the Atomic Energy Commission for providing partial support of this study.

SUMMARY

The feasibility of determining excitation spectra by means of a reflectance attachment for the Beckman DU Spectrophotometer has been demonstrated using aqueous solutions of dichlorofluorescein. Some differential measurements have also been made to explore further the applicability of the technique to analysis.

RÉSUMÉ

La possibilité de déterminer des spectres d'excitation, au moyen d'un dispositif de réflexion, d'un spectrophotomètre Beckman DU, a été démontrée, en utilisant des solutions aqueuses de dichlorofluorescéine. Quelques essais ont également été effectués pour appliquer cette technique à l'analyse.

ZUSAMMENFASSUNG

Die Möglichkeit Excitations-Spektren zu bestimmen mit Hilfe eines Reflektions-Dispositivs eines Spektrophotometers Beckman DU, wurde unter Verwendung von wässrigen Lösungen von Dichlorofluoreszein gezeigt. Einige Versuche wurden ebenfalls ausgeführt, um diese Analysentechnik anzuwenden.

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A CORRELATION CHART FOR SOLUTION CONCENTRATIONS MEASURED BY CIRCUITS WHOSE CONSTANTS ARE NOT IN AGREEMENT

by

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Since the author first suggested the application of radio-frequency to chemical analysis in 1936[1] and developed his heterodyne method and later his Q-metric and Rectified radio-frequency methods (in 1944)[2], a number of other workers have entered this field. Several variations of the original circuits have been developed and some new methods evolved[1-9]. In July 1954 having devised a simple low-frequency method of chemical analysis[10], he felt that some scheme of coordination was required to relate the micro-ammeter readings obtained by the various methods both to one another

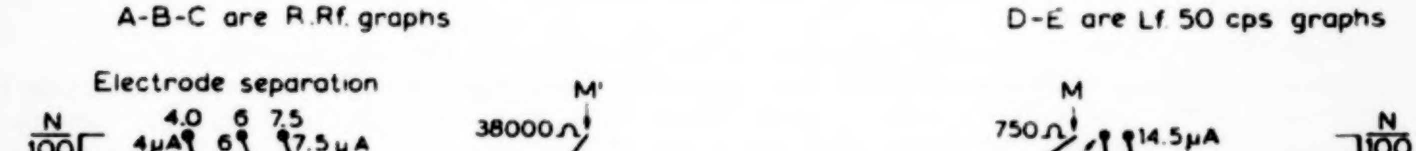

Fig. 1. Correlation Chart. This chart shows the relationship between measurements obtained by Q-metric, Rectified radio-frequency and Low-frequency a.c. methods and could be extended to embrace solutions at other temperatures and other methods of measurement.

Note: figure box approximate.

and to the standard specific resistances of the various solution concentrations. The problem was to find a simple method by which this could be achieved, bearing in mind that the circuit constants of each of the methods were different. In the case of the low-frequency method[10] for instance, the electrodes were in contact with the solution, whereas in each of the radio-frequency methods the electrodes were on the outside of the conductimetric tube[1]. The dimensions of the tubes, the electrodes and the distance separating the latter were all different.

CORRELATION CHART

The chart Fig. 1 enables the required relationships to be seen at a glance (this device of course could be employed also to correlate the measurements made by any other method used to obtain micro-ammeter deflections for solution concentrations).

Fig. 2 illustrates the circuit employed for plotting the three rectified radio-frequency (R. Rf.) graphs A, B and C*.

Fig. 3 is the low-frequency circuit by means of which graphs D and E were plotted[10].

Note that all the graphs which compose the chart were for stock solutions of potassium chloride at 22° C.**

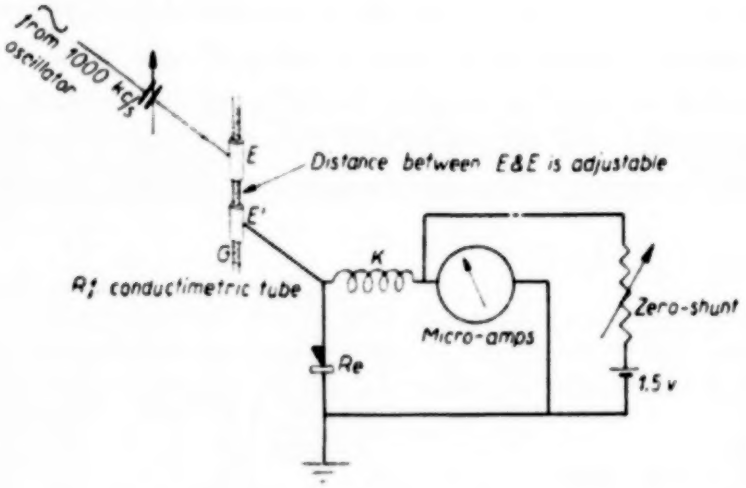

Fig. 2. This diagram illustrates the circuit by means of which the R. Rf. graphs A, B and C were plotted.
Electrodes E and E′ are on the outside of the glass conductimetric tube, G, containing the solution. Re is a germanium diode. K is a 2 μH radio-frequency choke.

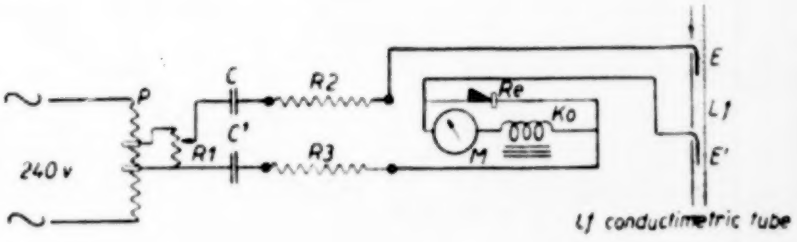

Fig. 3. This diagram shows the Lf. a.c. circuit (50 cps) by which the resistances of the various concentrations were measured, and by which curves D and E were plotted.
The components are as under: —

Re. is a germanium diode.
Ko „ „ Lf. Iron cored choke.
C and C′ are 2 μF condensers.
P is a 15000 ohm potential divider.

R′ is a 10,000 Ω Potentiometer.
R2 and R3 10,000 Ω Resistors.
M is a micro-ammeter.
Lf. is a low-frequency conductimetric tube with submerged electrodes E and E′.

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* For a detailed description refer to Ref. 1, 4 and 6, and to Ref. 7 for the method in which adjustable electrode separation is employed.

** In order not to complicate the chart the Standard resistance graph is given for only one temperature. On the original chart additional graphs were plotted for temperatures above and below 22° C.

The *ordinates* indicate the concentration and cover a range of from $N/1$ to $N/100$.

The *micro-ammeter deflection* appropriate to each graph for any selected concentration is indicated by the abscissae.

Graphs A, B and C were plotted by R. Rf., the electrodes on the conductimetric tube being a different distance apart in each case.

Graphs D and E were plotted by low-frequency using a low-frequency conductimetric tube[10].

Graph M. This specific resistance graph was plotted from the reciprocals of the conductivity of Standard solutions (Ref.[11], page 1894).

Graph M'. In this graph the resistances of small quantities of KCl solution contained in a low-frequency conductimetric tube of small diameter are plotted against their concentrations, hence the high values of the resistances recorded.

From graphs M and M' the relationship between the high-resistance measurements and the Standard resistance of any KCl solution can be seen immediately. For example: 30,500 ohms as measured on graph M' for $N/80$ KCl is equivalent to the Standard measurement of 600 ohms on graph M.

SUMMARY

This paper describes the employment of a graphic method to relate the various micro-ammeter deflections obtained for solution concentrations by radio-frequency, a.c. or d.c. methods, and also relates these measurements to the known standard specific resistance of the concentrations. Diagrams of the circuits employed and a reference list are given from which more complete details may be obtained.

RÉSUMÉ

Cet article décrit l'utilisation d'une méthode graphique, permettant de relier les concentrations de solutions avec les déflections d'un micro-ampèremètre, obtenues au moyen d'une méthode d'analyse par radiofréquence. Ces mesures sont également reliées aux résistances standard spécifiques connues des solutions, pour les mêmes concentrations. Les diagrammes des circuits et une liste de références sont donnés.

ZUSAMMENFASSUNG

Dieser Artikel beschreibt die Verwendung einer graphischen Methode, welche erlaubt die Konzentrationen der Lösungen mit den Ausschlägen eines Mikro-Ampermeters in Verbindung zu bringen, die man mit Hilfe einer Analysenmethode durch Radiofrequenz erhalten hat. Diese Messungen sind ebenfalls in Verbindung gebracht mit den bekannten speziefischen Standard-Widerständen der Lösungen für die gleichen Konzentrationen. Die Diagramme der Stromkreise und eine Liste von Referenzen sind gegeben.

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ÉTUDE DU COMPORTEMENT POLAROGRAPHIQUE DE Ge(IV)

par

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§ 1. INTRODUCTION

A l'heure actuelle, on possède peu de données au sujet du comportement polarographique de Ge(IV).

IVANOV-EMIN ET ALIMARIN[1] concluent de leur étude que le germanium tétravalent n'est pas réductible, ni en milieu acide, ni en milieu alcalin. DAS GUPTA ET NAIR[2], au contraire, observent une double vague en milieu NH_4OH-NH_4Cl et ils affirment qu'il s'agit de la réduction en deux stades du germanium tétravalent à l'état métallique.

Nous nous proposons de donner les résultats d'une étude systématique de la réduction de Ge(IV) dans un milieu KCl tamponné et dans le milieu NH_4Cl-NH_4OH et nous montrerons dans quelles conditions la vague polarographique peut servir à l'analyse.

§ 2. DÉTAILS EXPÉRIMENTAUX

Tous les polarogrammes ont été enregistrés au polarographe Sargent modèle XXI. Le relevé précis de la vague destiné à l'établissement de l'équation, a été fait au moyen d'un appareil manuel. Toutes les mesures ont été effectuées à 25° ± 0.1 C. Les pH ont été mesurés au pH-mètre radiometer. Toutes les solutions sont préparées à partir d'une solution stock, $2.5 \cdot 10^{-3} M$ en germanium (0.1307 g de GeO_2 dans 500 ml d'eau).

§ 3. RÉSULTATS EXPÉRIMENTAUX

A. Etude du comportement polarographique de Ge(IV) en milieu tamponné et en présence de KCl

(1) Influence de la concentration en KCl

Les résultats sont mentionnés dans le Tableau I.

TABLEAU I

Ge: $0.25 \cdot 10^{-3} M$; solution tampon: H_3BO_3 0.1 M + NaOH 0.1 N.
$m^{2/3}t^{1/6}$ = 2.44 Damping: 1.

pH	8.95	8.97	8.94	8.92	8.81	8.91	8.88	8.90	8.95
Concentration en KCl mole/litre	—	0.025	0.05	0.10	0.50	1.00	1.50	2.00	3.00
i_d en μA	3.93	4.04	4.07	4.16	4.72	5.22	5.84	6.00	6.28
$E^1/_2$ volts v/SCE	—1.51	—1.485	—1.48	—1.46	—1.425	—1.420	—1.410	—1.420	—1.410

Nous constatons, pour des solutions dont la concentration en KCl est supérieure à 0.1*M* et en l'absence de gélatine, une augmentation de la vague avec la concentration en KCl.

(2) Influence de la présence de gélatine

Le Tableau II donne les résultats obtenus en présence de 0.01% de gélatine.

TABLEAU II

Ge: $0.25 \cdot 10^{-3} M$; solution tampon H_3BO_3 0.1*M* + NaOH 0.1*N*
$m^{2/3}t^{1/6} = 2.44$ Damping: 1

pH	8.88	8.90	8.90	8.94	8.95
Concentration en KCl mole/litre	2.00	1.00	0.50	0.10	0.05
i_d en μA	4.23	4.24	4.24	4.18	4.13
$E^1/_2$ en volts *v*/SCE	—1.455	—1.460	—1.460	—1.485	—1.495

On voit que l'addition de gélatine supprime l'effet exaltant du KCl en forte concentration sur la hauteur de la vague de réduction du germanium.

ORLEMANN ET KOLTHOFF[3,4] ont signalé un phénomène du même genre, dans la réduction du zinc et ils l'attribuent à la réduction de l'eau adsorbée à la surface de l'électrode.

Tous les essais ultérieurs ont été effectués en présence de KCl 0.05*M* et de 0.01% de gélatine.

(3) Influence du pH sur la hauteur de la vague

Nous avons ensuite examiné la réduction à différents pH, en milieu tamponné et en présence de KCl. Les résultats de ces essais sont rassemblés dans le Tableau III et reproduits dans la Fig. 1. On voit que l'influence du pH du milieu se fait sentir à la fois sur la hauteur de la vague et sur le potentiel de demi-vague; il en résulte que, du point de vue analytique, les essais devront se faire dans une zone étroite de pH allant de 8 à 9 où la hauteur est constante.

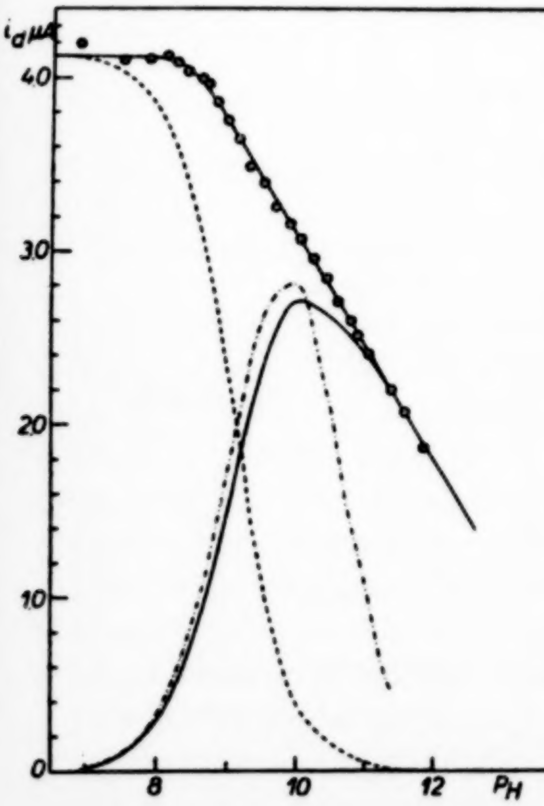

Fig. 1. $c = 0.25 \cdot 10^{-3} M$ en Ge, 0.01% en gélatine, KCl 0.05*M*. $m^{2/3}t^{1/6} = 2.40$
——o——: valeurs expérimentales.
— — — — —: courbe théorique de réduction de H_2GeO_3 en Ge°.
————————: courbe expérimentale du courant cinétique.
—·—·—·—: courbe théorique du courant cinétique.

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TABLEAU III

Ge: $0.25 \cdot 10^{-3} M$; KCl $0.05 M$ + 0.01% gélatine

pH	*Tampon*	i_d *en* μA	$E^1/_2$ *volts v/SCE*
8.11	Na_2CO_3 $0.1 M$ + H_3BO_3 $0.1 M$	4.12	—1.500
8.26	,, ,, + ,, ,,	4.10	—1.500
8.41	,, ,, + ,, ,,	4.02	—1.505
8.60	,, ,, + ,, ,,	4.00	—1.507
8.76	,, ,, + ,, ,,	3.96	—1.510
8.97	,, ,, + ,, ,,	3.76	—1.510
9.18	,, ,, + ,, ,,	3.64	—1.515
9.31	,, ,, + ,, ,,	3.50	—1.522
9.51	,, ,, + ,, ,,	3.40	—1.540
9.70	,, ,, + ,, ,,	3.26	—1.555
9.88	,, ,, + ,, ,,	3.16	—1.570
10.06	,, ,, + ,, ,,	3.08	—1.582
10.47	,, ,, + ,, ,,	2.96	—1.590
10.62	,, ,, + ,, ,,	2.85	—1.622
10.80	,, ,, + ,, ,,	2.62	—1.645
10.90	,, ,, + ,, ,,	2.52	—1.660
11.05	$Na_2HPO_4.2H_2O$ $0.1 M$ + NaOH $0.1 N$	2.40	—1.675
11.20	,, ,, + ,, ,,	2.36	—1.695
11.41	,, ,, + ,, ,,	2.20	—1.710
11.60	,, ,, + ,, ,,	2.08	—1.725
11.80	,, ,, + ,, ,,	1.86	—1.760

$(m^{2/3}t^{1/6})$ à —1.66 volt = 2.40; $(m^{2/3}t^{1/6})$ à —1.80 volt = 2.39
$(m^{2/3}t^{1/6})$ à —1.74 volt = 2.40; $(m^{2/3}t^{1/6})$ à —1.84 volt = 2.37

Remarque: Vu la faible variation de $(m^{2/3}t^{1/6})$ avec le potentiel où on mesure i_d, (écart inférieur à 2%), nous n'avons pas corrigé les valeurs de i_d.

(4) *Proportionnalité entre i_d et la concentration en germanium*

Les résultats obtenus sont donnés dans le Tableau IV.

TABLEAU IV

Milieu: KCl $0.05 M$. Tampon: NaOH $0.1 N$ + H_3BO_3 $0.1 M$
m = 3.14 mg sec^{-1} t = 2.20 sec
$(m^{2/3}t^{1/6})$ à —1.70 volt = 2.44

Concentration Ge	*pH*	i_d *en* μA	$K = \dfrac{i_d}{m^{2/3}+t^{1/6}C}$	$E^1/_2$ *volts v/SCE*
$0.625\ 10^{-3} M$	8.90	10.50	6.90	1.520
0.500 ,,	8.90	8.32	6.82	1.520
0.425 ,,	8.90	7.12	6.86	1.510
0.3125 ,,	8.93	5.19	6.82	1.500
0.250 ,,	8.93	4.16	6.82	1.500
0.175 ,,	8.94	2.94	6.88	1.500
0.125 ,,	8.93	2.07	6.80	1.500
0.0625 ,,	8.93	1.02	6.70	1.500
			K moyen = 6.82 ± 0.04	

Dans les limites des erreurs de mesures, la proportionnalité entre la hauteur de la vague et la concentration est vérifiée.

(5) Influence de la hauteur du mercure

L'influence de la pression de mercure sur la hauteur de la vague permet de décider si le courant limite est contrôlé par la diffusion ou par la cinétique d'une réaction.

Les résultats des mesures effectuées à pH 8.9 sont rassemblés dans le Tableau V.

TABLEAU V

Ge: $0.425 \cdot 10^{-3} M$; Milieu: KCl $0.050 M$; tampon: H_3BO_3 $0.1 M$ + NaOH $0.1 N$; pH = 8.90 et 0.01% en gélatine

h_{cm}	$m_{mg/sec}$	t_{sec}	$P_{back} = \frac{3.1}{(mt)^{1/2}}$	h corrigé cm	$i_{d\mu A}$	$\frac{i_d}{(h\ corr)^{1/2}}$
15.80	1.53	4.28	1.65	14.17	5.04	1.34
24.00	2.42	2.77	1.64	22.37	6.24	1.32
30.70	3.14	2.16	1.63	29.07	7.04	1.30
39.20	4.03	1.71	1.63	37.57	7.92	1.29
49.00	5.16	1.34	1.63	47.37	8.80	1.28
56.00	5.74	1.20	1.63	54.37	9.36	1.27
64.00	6.75	1.02	1.63	62.37	10.00	1.27
72.10	7.50	0.92	1.63	70.47	10.48	1.25
79.70	8.30	0.83	1.63	78.07	11.04	1.245
85.50	8.96	0.77	1.63	83.87	11.36	1.24
			$P_{back} = 1.63$			

Pour une vague pure de diffusion, on observe, en accord avec la théorie[5], une diminution de $\frac{i_d}{h^{1/2}}$ lorsque *h* augmente, suivie d'une légère augmentation provoquée par l'agitation aux débits élevés, lorsque *t* atteint des valeurs inférieures à 1.50 sec.

Dans ce cas ci, la décroissance de $\frac{i_d}{h^{1/2}}$ est continue et il est probable que ce soit l'indice d'un faible courant cinétique; au pH = 9,80, on observe le même phénomène.

(6) Discussion des résultats

La valeur de la constante de diffusion $K = 6.82$ permet de calculer le nombre d'électrons intervenant dans la réaction d'électrode; en adoptant une valeur probable de $D = 10^{-5} cm^2/sec$, on trouve que $n = 3.51$. Ce résultat montre que dans les conditions expérimentales du Tableau IV, la vague correspond à la réduction du germanium tétravalent à l'état métallique ($n = 4$).

Dans ces conditions, le coefficient de diffusion vaut $0.79 \cdot 10^{-5} cm^2/sec$.

L'étude de l'équation de la vague de réduction au pH 8.90 montre clairement que la réaction est irréversible; le coefficient angulaire trouvé vaut 0.084 à la place de 0.0147 pour une vague réversible.

Le résultat le plus surprenant que nous ayons observé est sans doute la diminution progressive du courant de diffusion avec le pH du milieu: CARPINI[6] a montré qu'en solution diluée, le germanium se trouve sous forme de H_2GeO_3, acide faible, avec les p*K*

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respectifs de 9.1 et 12.7. On peut donc se demander si la diminution du courant de diffusion observée n'est pas attribuable simplement à une diminution de concentration de la forme réductible qui serait dans ce cas H_2GeO_3.

Si l'on calcule la concentration en H_2GeO_3 en fonction du pH, on peut tracer une courbe théorique du courant de diffusion (i_d) H_2GeO_3. On constate que les valeurs expérimentales sont toujours plus grandes et la courbe en cloche représentant la différence entre les valeurs expérimentales et les valeurs de (i_d) H_2GeO_3 rappelle fortement celle d'un courant cinétique: le courant total observé serait égal à la somme de (i_d) H_2GeO_3 (courant de diffusion des molécules H_2GeO_3 existant au sein de la solution) et d'un courant cinétique i_K (provenant des molécules H_2GeO_3 formés au sein de la couche de diffusion par réaction $H^+ + HGeO_3^- \rightarrow H_2GeO_3$).

Brdicka[7] a fait une théorie du phénomène et il a montré que

$$\frac{1}{\mu k} = \frac{[H^+]\ nFq}{a}\left[\frac{a.c.K.}{i_K\,(K+H^+)} - 1\right] \quad \ldots\ldots\ldots\ldots (1)$$

μ: épaisseur de la couche dans laquelle la réaction de formation de H_2GeO_3 s'opère.
q: surface moyenne de la goutte de mercure.
a: constante du courant de diffusion de l'équation d'Ilkovic.
c: concentration globale en germanium.
K: concentration d'équilibre de dissociation de H_2GeO_3 $K = 10^{-9.1}$.
k: constante de vitesse de la réaction $H^+ + HGeO_3^- \rightarrow H_2GeO_3$. Si l'on effectue le calcul à partir de la valeur de $a.c. = 4.12\ \mu A$, on trouve aux différents pH, les valeurs suivantes pour $\frac{1}{\mu k}$ (Tableau VI).

TABLEAU VI

pH	$\frac{1}{\mu k}$ *(mole/litre sec) cm*$^{-1}$
8.50	$2.6 \cdot 10^{-7}$
9.00	$1.27 \cdot 10^{-7}$
10.00	$2.08 \cdot 10^{-8}$
11.00	$4.40 \cdot 10^{-9}$

Comme on peut s'en rendre compte, la valeur trouvée pour $\frac{1}{\mu k}$ est loin d'être constante; pour se faire une idée de l'accord des résultats expérimentaux avec la théorie du courant cinétique, nous avons calculé la courbe théorique $(i_K)_{\text{théor.}}$ à partir de la valeur de $\frac{1}{\mu k} = 2 \cdot 10^{-8}$ et de l'équation (1).

Cette courbe se trouve dans la Fig. 1. On remarque que l'accord est satisfaisant jusqu'au pH = 10 mais qu'au delà, la courbe théorique du courant cinétique diminue beaucoup plus rapidement que la courbe expérimentale. Étant donné que le palier de diffusion de la vague du germanium est assez mal défini, il est probable que le courant i_d mesuré comprend une fraction du courant résiduel et dans ces conditions, l'erreur en excès sur le courant réel de diffusion doit augmenter avec le pH. Le fait explique probablement les écarts observés aux pH > 10.

B. Comportement polarographique de Ge(IV) en milieu $NH_4Cl + NH_4OH$

Nous avons signalé dans l'introduction que Das Gupta et Nair ont observé pour

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Ge(IV) en milieu NH_4Cl 0.5M + NH_4OH 0.5M une vague double qu'ils attribuent à la réduction du germanium en deux stades. Il nous a paru intéressant de reprendre cette étude étant donné qu'il n'est pas exclu que la première vague soit due à la réduction de H_2GeO_3 et que la seconde provienne de la réduction de $[HGeO_3^-]$.

Dans ces conditions, on devrait observer un changement de la hauteur relative des deux vagues en fonction du pH.

Ces considérations nous ont amené à étudier l'influence des différents paramètres suivants:

(1) *Influence de la concentraction en germanium*

Le Tableau VII contient les données expérimentales obtenues: hauteurs et potentiels $E^1/_2$ des deux vagues, ainsi que la valeur des constantes du courant de diffusion.

TABLEAU VII

NH_4Cl: 0.5M + NH_4OH: 0.5M pH = 9.40
gélatine: 0.02% m = 2.74 mg sec^{-1}
t = 2.42 sec $(m^{2/3}t^{1/6})$ à —1.7 volt v/SCE = 2.27
$(m^{2/3}t^{1/6})$ à —1.8 volt v/SCE = 2.22

Concentration Ge	$(i_d)_1$ µA	$K_1 = \frac{i_{d1}}{m^{2/3}t^{1/6}.C}$	$(E^1/_2)_1$ volt v/SCE	$(i_d)_2$ µA	$K_2 = \frac{i_{d2}}{m^{2/3}t^{1/6}.C}$	$(E^1/_2)_2$ volt v/SCE	i_d *total* µA
0.625·$10^{-3}M$	10.42	7.34	—1.560	7.50	5.40	—1.790	17.92
0.500 ,,	8.30	7.31	—1.560	6.20	5.58	—1.790	14.20
0.425 ,,	6.90	7.15	—1.560	5.65	6.00	—1.780	12.55
0.3125 ,,	5.10	7.20	—1.560	4.80	6.92	—1.770	9.90
0.250 ,,	4.00	7.10	—1.560	4.24	7.64	—1.775	8.24
0.175 ,,	2.91	7.34	—1.560	3.42	8.80	—1.750	6.33
0.125 ,,	2.00	7.05	—1.560	2.90	10.45	—1.740	4.90
0.0625 ,,	1.04	7.34	—1.565	1.84	13.28	—1.740	2.88
		K_{moyen} = 7.23 ± 0.10 avec $m^{2/3}t^{1/6}$ = 2.27			avec $m^{2/3}t^{1/6}$ = 2.22		

La première vague a, dans les limites des erreurs expérimentales, une hauteur proportionnelle à la concentration en germanium et la constante du courant de diffusion est du même ordre de grandeur que celle trouvée pour la vague du germanium en milieu KCl tamponné. Il n'existe au contraire aucune proportionnalité pour la seconde vague.

(2) *Influence du pH du milieu*

Nous avons ensuite modifié le pH du milieu en faisant varier le rapport $\frac{NH_4OH}{NH_4Cl}$, pour une concentration constante en ammonium égale à 1.0M.

On observe d'après les résultats du Tableau VIII que, comme dans le milieu KCl, la hauteur des vagues diminue lorsque le pH du milieu augmente.

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TABLEAU VIII

Ge: $0.25 \cdot 10^{-3} M$
Milieu: $NH_4Cl + NH_4OH$. Concentration totale en $NH_4^+ = 1.0 M$
Gélatine: 0.02%

pH	*concentration en $NH_3(M)$*	*concentration en NH_4 (M)*	*$(i_d)_1$ en μA*	*$(id)_2$ en μA*	*(i_d) total μA*	*$(E^{1}/_{2})_1$ volt v/SCE*	*$(E^{1}/_{2})_2$ volt v/SCE*
8.48	0.10	0.90	4.40	5.68	10.08	—1.540	—1.755
8.82	0.20	0.80	4.24	5.12	9.36	—1.560	—1.770
9.05	0.30	0.70	4.12	4.88	9.00	—1.565	—1.775
9.25	0.40	0.60	4.00	4.52	8.52	—1.575	—1.770
9.40	0.50	0.50	3.96	4.24	8.20	—1.575	—1.775
9.59	0.60	0.40	3.84	4.16	8.00	—1.580	—1.780
9.75	0.70	0.30	3.72	4.16	7.88	—1.605	—1.800
9.95	0.80	0.20	3.64	4.12	7.76	—1.620	—1.810
10.25	0.90	0.10	3.36	4.00	7.36	—1.625	—1.800

(3) Influence de la concentration totale en tampon ammonique

Nous avons constaté qu'en diminuant progressivement la concentration en tampon NH_4OH-NH_4Cl, la hauteur de la seconde vague diminue pour disparaître pour une concentration inférieure à $0.5 M$; la hauteur de la première vague diminue également légèrement avec une diminution de la concentration en NH_4^+.

(4) Discussion

De l'ensemble de ces deux résultats, nous pouvons conclure que contrairement à l'opinion émise par DAS GUPTA ET NAIR, seule la première des deux vagues observées correspond à la réduction du Ge(IV) à l'état métallique, puisque:

1. la constante du courant de diffusion est en accord avec $n = 4$.
2. la première vague est proportionnelle à la concentration en germanium.
3. la seconde vague disparaît lorsque la concentration en électrolyte support diminue.

D'autre part, notre hypothèse de départ ne se trouve pas vérifiée non plus et il est vraisemblable que la seconde vague soit encore une fois apparentée au „courant d'eau".

TABLEAU IX

Teneur en Zn en %	*Teneur en Ge donnée en %*	*Teneur en Ge trouvée en %*	*Erreur relative en %*
99.00	1.00	1.02	+2.00
99.00	1.00	1.05	+5.00
99.05	0.95	0.94	+1.05
99.05	0.95	0.93	+2.10
99.05	0.95	0.94	+1.05
99.50	0.50	0.506	+1.20
99.80	0.20	0.201	+0.50
99.90	0.10	0.108	+8.00

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C. Application analytique

L'existence de la vague de réduction de Ge(IV) peut être mise à profit pour son dosage; les conditions les plus favorables sont les suivantes:
KCl 0.05*M*, tampon H_3BO_3 0.1*M* + NaOH 0.1*M* donnant un pH compris entre 8 et 9 (ce pH peut être fixé au moyen du bleu de xylénol comme indicateur).

Nous avons montré que le dosage polarographique du germanium est possible en présence de fortes concentrations en zinc, en ayant soin d'ajouter du complexon; dans ces conditions, la vague de réduction du zinc est rejetée au delà de —2.00 volts tandis que celle du germanium n'est pas affectée.

Le Tableau IX contient quelques résultats.

Lorsqu'il y a en solution d'autres ions gênant la polarographie du germanium, on peut songer à commencer par une séparation par extraction de $GeCl_4$ dans CCl_4[9]; des essais dans cette voie sont actuellement en cours.

Nous tenons à remercier Monsieur le PROFESSEUR G. DUYCKAERTS pour l'aide et l'intérêt constant qu'il n'a cessé de porter à ce travail.

RÉSUMÉ

A des pH supérieurs à 7, on observe une vague de réduction de Ge(IV). L'étude de la vague a montré que la réduction est irréversible et se fait de Ge^{+4} à Ge° et que sa hauteur dépend fortement du pH. Nous avons montré que la seconde vague observée par DAS GUPTA ET NAIR dans le milieu NH_4Cl — NH_4OH ne peut être attribuée au germanium. Du point de vue analytique, il y a lieu de se placer dans la zone de pH de 8 à 9 où la hauteur de la vague peut être considérée comme constante; la constante du courant de diffusion vaut 6.82. Dans le milieu KCl 0.05*M*, la valeur de D = $0.79 \cdot 10^{-5}$ cm²/sec et $E^{1/2}$ = —1.50 volt *v*/SCE; tandis qu'en milieu NH_4Cl-NH_4OH, D = $0.89 \cdot 10^{-5}$ cm²/sec et $E^{1/2}$ = —1.56 volt *v*/SCE.

SUMMARY

A reduction wave of Ge(IV) is observed at pH valvest greater than 7. The study of the wave has shown that the reduction is irreversible and occurs from Ge^{+4} to Ge° and that its height is strongly dependend on the pH. We have shown that the second wave observed by DAS GUPTA AND NAIR in the medium NH_4Cl-NH_4OH cannot be ascribed to Ge. From an analytical point of view, it should be operated in the pH-region from 8 to 9, where the height of the wave can be considered as constant; the diffusion current constant equals 6.82. In the KCl 0.05*M* medium, we have measured D = $0.79 \cdot 10^{-5}$ cm²/sec and $E^{1/2}$ = —1.50 volt *v*/SCE; whereas in the NH_4Cl-NH_4OH medium, D = $0.89 \cdot 10^{-5}$ cm²/sec and $E^{1/2}$ = —1.56 volt *v*/SCE.

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Für pH-Werte höher als 7, stellt man eine Reduktionswelle des Ge(IV) fest. Das Studium der Stufe zeigt, dass die Reduktion irreversibel ist und von Ge^{+4} bis Ge° stattfindet und schliesslich die Stufenhöhe sehr stark vom pH abhängig ist. Wir haben ebenfalls gezeigt, dass die zweite Stufe im NH_4Cl-NH_4OH-Medium, von DAS GUPTA UND NAIR beobachtet, nicht dem Germanium zuzuschreiben ist. Für analytische Zwecke, muss man den pH-Bereich 8 bis 9 benutzen, wo die Stufenhöhe als ständig betrachtet ist; die Diffusionsstromkonstante ist 6.82. Im KCl 0.05*M*-Medium gilt D = $0.79 \cdot 10^{-5}$ cm²/sec und $E^{1/2}$ = —1.50 volt *v*/SCE; während im NH_4Cl-NH_4OH Medium, D = $0.89 \cdot 10^{-5}$ cm²/sec und $E^{1/2}$ = —1.56 volt *v*/SCE.

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BOOK REVIEW

Isotopic Gas Analysis for Biochemists, by R. F. **Glascock**, Academic Press Inc., New York, 1954, 247 pages, 74 figures.

The author of this book is Head of the Isotope Section at the National Institute for Research in Dairying, University of Reading, England and has been concerned with the gas phase measurement of carbon and hydrogen isotopes in samples of biochemical and physiological interest. The main emphasis, therefore, is given to a full description of the apparatus for and use of the permanent vacuum line technique for the assay of carbon-14 and tritium.

After a brief outline of radioactive assay methods there follow chapters on high vacuum apparatus, gas phase assay of carbon-14, combustion of labelled compounds, the determination of deuterium and of tritium, the preparation of heavy nitrogen samples for mass spectrometric analysis and the preparation of tritium labelled compounds.

The book is a mine of valuable detailed information on vacuum line operation and gas phase counting. The author condenses and imparts his experience in a most valuable manner and illustrates his recommended equipment with very clear diagrams. This book can be recommended not only to biochemists but to anyone interested in the handling and counting of radioactive gases.

A. A. **Smales** (Harwell)

REVUE DE LIVRE

Analyse Quantitative Minérale par **Gaston Charlot et Denise Bézier**, Masson et Cie, Paris, 1955, 823 pages, prix Fr. franç, 7.000.

La troisième édition de ce traité vient de sortir de presse. Il a été profondément remanié. La première partie qui, sous le nom de ,,Méthodes générales d'analyse'' comprend la partie théorique et la partie instrumentale, a été particulièrement développée. On y trouve entre autres un important chapitre sur la colorimétrie qui renferme tous les éléments utiles à l'analyste: appareillage, lois fondamentales, précision des dosages, conditions pratiques de ceux-ci, etc. Il se termine par un paragraphe sur la titration colorimétrique.

Les méthodes d'électroanalyse sont vues sous un jour tout nouveau et fort attachant. Partant des courbes de polarisation, le Professeur **Charlot** et sa collaboratrice nous amènent de façon fort claire à l'électrolyse, à la polarographie, à la potentiométrie, à l'ampérométrie et à la coulométrie. Remarquable exposé basé sur les conceptions les plus modernes de la physico-chimie qui apporte beaucoup de clarté dans un domaine compliqué où règne souvent une grande confusion.

La plupart des chapitres de cette première partie ont subi un important développement, tels par exemple: les méthodes statistiques, les séparations, le dosage dans les solvants non aqueux, la chromatographie, l'analyse des gaz . . .

La seconde partie de cet ouvrage traite des dosages des principaux éléments. On y trouve en outre les séparations fondamentales, les méthodes d'analyse classiques et physico-chimiques avec une brève description des plus importantes d'entre álles et une bibliographie très complète qui va jusqu'en 1953.

Pour apprécier toute la valeur de cet ouvrage, il est nécessaire de connaître les bases de la chimie générale: aussi n'est-il pas destiné aux débutants.

Remarquable en tout point, à l'avant-garde du progrès, clair et concis, extrêmement bien documenté, le Traité de **Charlot et Bézier** est l'un des meilleurs parus au cours de ces dernières années sur la chimie analytique.

D. **Monnier** (Genève)

SODIUM META-VANADATE AS VOLUMETRIC REAGENT

IV. IODINE MONOCHLORIDE METHOD

by

BALWANT SINGH AND SARWAN SINGH

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SIROKOMSKI AND KLIMENKOV[1] used ammonium meta-vanadate for the volumetric estimation of iron, molybdenum and copper using phenanthranilic acid as indicator.

GOPALA RAO and co-workers[2] showed that sodium vanadate has special advantages over potassium permanganate and dichromate as a volumetric reagent. It can be used for the estimation of ferrous salts in presence of oxalic acid, citric acid, alcohols and phenols, where potassium permanganate, potassium dichromate and even ceric sulphate give too high results. They used sodium vanadate for the volumetric estimation of ferrocyanide alone and in the presence of hydrochloric acid and oxalic acid, hydroquinone in the presence of some phenolic compounds, uranium, tartaric acid, indigo and indigo carmine, using diphenylbenzidine as an internal indicator.

B. SINGH AND R. SINGH[3] used sodium meta-vanadate as a volumetric reagent for the direct determination of potassium iodide, sodium arsenite, mercurous chloride, potassium thiocyanate, sodium sulphite, sodium bisulphite, sodium thiosulphate, ferrous sulphate and hydrazine sulphate, and for the indirect determination of hydrogen peroxide, lead dioxide, manganese dioxide, selenium dioxide, potassium persulphate, copper sulphate, sodium formate and sodium sulphide, by the iodine monochloride method.

In the present investigation an attempt has been made to determine copper, zinc, cobalt, mercury and lead by the iodine monochloride method, using sodium meta-vanadate as volumetric reagent. Cu^{+2}, Zn^{+2} and Co^{+2} were precipitated as complex mercurythiocyanates, Hg^{+2} as zinc mercurythiocyanate and Pb^{+2} was precipitated as iodide. In acid media the thiocyanates and the iodides react with sodium meta-vanadate in accordance with the equations:

$$[Hg(CNS)_4]^{-2} + 24\,VO_3^- + 64H^+ = Hg^{+2} + 4\,CN^- + 4\,SO_4^{-2} + 24\,VO^{+2} + 32\,H_2O$$

$$I^- + 2\,VO_3^- + 8H^+ = I^+ + 2\,VO^{+2} + 4\,H_2O$$

In all titrations with sodium meta-vanadate, 5 ml of 0.02*M* iodine monochloride, 5 ml of chloroform and sufficient hydrochloric acid to keep the normality between 7.0 and 7.5*N* were added to the titrant in a conical flask. In titrations of the iodides with sodium meta-vanadate, iodine monochloride was not added to the titrant because of its formation during the titration. Sodium meta-vanadate was added from a burette until the solution, which was coloured with iodine, became pale green. The conical flask was then stoppered and vigorously shaken. Addition of small volumes of the meta-vanadate solution was continued, shaking vigorously after each addition until the chloroform layer was faintly violet. The reagent was then added dropwise, with shaking after the addition of each drop, until the chloroform layer changed its colour from violet to light pale yellow. The end-point was very sharp.

Determination of copper, zinc and cobalt

A known amount of each substance was dissolved in water and the solution acidified with dilute hydrochloric acid. Each metal was precipitated from its salt solution as metallic mercury thiocyanate with a reagent which contained 39.0 g of ammonium thiocyanate and 27.0 g of mercuric chloride per litre. The precipitate was allowed to stand for three hours, filtered and washed thoroughly with a wash-liquid composed of 5 ml of the precipitating reagent and 450 ml of water. Finally, the precipitate was washed once with a little water to remove the adhering wash-liquid. The precipitate along with the filter paper was transferred to a conical flask, dissolved in about 30 ml of concentrated hydrochloric acid and titrated against standard sodium meta-vanadate solution in presence of iodine monochloride and chloroform. The results are recorded in the following Tables:

TABLE I

COPPER SULPHATE

$CuSO_4.5H_2O$ *taken*	$0.10N$ $NaVO_3$ *used*	$CuSO_4.5H_2O$ *found*
g	ml	g
0.0154	15.00	0.0156
0.0206	20.00	0.0208
0.0311	30.00	0.0312
0.0416	40.00	0.0416
0.0520	50.00	0.0520

TABLE II

ZINC SULPHATE

$ZnSO_4.7H_2O$ *taken*	$0.10N$ $NaVO_3$ *used*	$ZnSO_4.7H_2O$ *found*
g	ml	g
0.0115	9.80	0.0117
0.0179	15.10	0.0181
0.0238	20.00	0.0239
0.0297	25.00	0.0299
0.0358	30.00	0.0359

TABLE III

COBALT CHLORIDE

$CoCl_2.6H_2O$ *taken*	$0.10N$ $NaVO_3$ *used*	$CoCl_2.6H_2O$ *found*
g	ml	g
0.0197	20.00	0.0198
0.0253	25.60	0.0254
0.0301	30.40	0.0301
0.0397	40.00	0.0396
0.0496	50.00	0.0496

Determination of mercury

A known amount of mercuric chloride was dissolved in 100 ml of water containing a few drops of hydrochloric acid. About 25 ml of ammonium thiocyanate-zinc sulphate reagent, which contained 39.0 g of ammonium thiocyanate and 29.0 g of zinc sulphate, were added in order to precipitate mercury as mercuric zinc thiocyanate. The precipitate was allowed to stand for three hours, filtered, washed thoroughly with a wash-liquid containing 5 ml of the precipitating reagent and 450 ml of water, and finally washed with a little water. The precipitate along with the filter paper was transferred to a conical flask, dissolved in about 25 ml of concentrated hydrochloric acid and titrated against standard sodium meta-vanadate solution in presence of iodine monochloride and chloroform. The results are given in Table IV.

TABLE IV

MERCURIC CHLORIDE

$HgCl_2$ taken	*0.10N $NaVO_3$ used*	*$HgCl_2$ found*
g	ml	g
0.0119	10.50	0.0119
0.0237	20.80	0.0235
0.0395	34.65	0.0392
0.0452	39.90	0.0451
0.0508	44.95	0.0508

Determination of lead

A known amount of lead nitrate was dissolved in water. The solution was treated with excess of potassium iodide and allowed to stand for six hours. The precipitated lead iodide was filtered and washed with cold water. The precipitate along with the filter paper was transferred to a conical flask, dissolved in a minimum amount of 1% sodium hydroxide solution. The solution was acidified with 20 ml of concentrated hydrochloric acid and titrated against standard sodium meta-vanadate solution in presence of chloroform. The results are recorded in Table V.

TABLE V

LEAD NITRATE

$Pb(NO_3)_2$ taken	*0.10N $NaVO_3$ used*	*$Pb(NO_3)_2$ found*
g	ml	g
0.0915	11.05	0.0915
0.1830	22.10	0.1830
0.2484	30.00	0.2484
0.3312	40.00	0.3312
0.3726	45.00	0.3726

SUMMARY

In hydrochloric acid medium sodium meta-vanadate was used as a volumetric reagent for the determination of copper, zinc, cobalt, mercury, and lead. Cu^{+2}, Zn^{+2} and Co^{+2} were precipitated as complex mercurythiocyanates, Hg^{+2} as mercuric zinc thiocyanate and Pb^{+2} as iodide. The thiocyanates were dissolved in concentrated hydrochloric acid and titrated against standard sodium meta-vanadate solution in the presence of iodine monochloride as a pre-oxidizer and catalyst. In titration of the iodide against the meta-vanadate, it was not necessary to add

iodine monochloride to the titrant because it is formed during the titration. Chloroform was used as an indicator. It was pink owing to the liberation of iodine during the titration and became pale yellow at the end-point because of the formation of iodine monochloride.

RÉSUMÉ

Le métavanadate de sodium peut être utilisé pour le dosage volumétrique du cuivre, du zinc, du cobalt, du mercure et du plomb. Cu^{+2}, Zn^{+2} et Co^{+2} sont précipités comme mercurithiocyanates, Hg^{+2} comme mercurithiocyanate de zinc; Pb^{+2} comme iodure. Les thiocyanates sont ensuite dissous dans l'acide chlorhydrique concentré et titrés par une solution étalon de métavanadate de sodium, en présence de monochlorure d'iode comme préoxydant et catalyseur. Dans le cas des titrations d'iodures par le métavanadate, il est inutile d'ajouter du monochlorure d'iode, puisqu'il s'en forme pendant la titration. Le chloroforme est utilisé comme indicateur. Il se colore en violet par l'iode libéré pendant la titration et devient jaune pâle au point final par formation de monochlorure d'iode.

ZUSAMMENFASSUNG

Das Natriummetavanadat kann für die volumetrische Bestimmung von Kupfer, Zink, Kobalt, Quecksilber und Blei verwendet werden. Cu^{+2}, Zn^{+2} und Co^{+2} werden als Merkurithiocyanat, Hg^{+2} als Zinkmerkurithiocyanat, Pb^{+2} als Jodide ausgefällt. Die Thiocyanate werden darauf in konzentrierter Salzsäure aufgelöst und mit einer Vergleichslösung von Natriummetavanadat, in Gegenwart von Jodmonochlorid als voroxydierendes Mittel und Katalysator titriert. Im Falle der Titrationen der Jodide mit Metavanadat, ist es nicht notwendig Jodmonochlorid dazuzugeben, da es sich während der Titration bildet. Chloroform wird als Indikator verwendet. Es färbt sich violett durch das während der Titration freigewordene Jod und wird hellgelb beim Umschlagspunkt der Bildung von Jodmonochlorid.

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RAPID TITRIMETRIC DETERMINATION OF MICROGRAM AMOUNTS OF FLUORIDE ION WITH SPADNS -THORIUM LAKE

by

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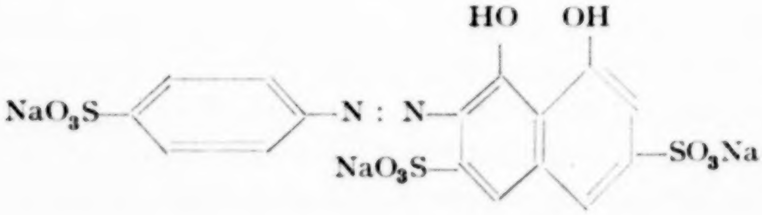
INTRODUCTION

A number of chelation compounds (lakes) of thorium[1-2] and zirconium[3] has been recently utilized for the spectrophotometric determination of fluoride ion in small concentrations. Fluoride ions form very stable complex ions with thorium and zirconium and react to displace the dye molecules. These methods thus involve the bleaching of the coloured lakes in the course of their reaction with fluoride ions and the subsequent liberation of the free dyes. In this way, quantitative determinations of fluoride ions are made by measuring the ratio of the displaced free dye to the colour of the unchanged lake.

Direct titrimetric methods for the estimation of fluorine are also mentioned in the literature. The method of WILLARD AND WINTER[4] involves a tedious titration in which the thorium-alizarin end point must be approached with great care. MILTON AND LIDDEL[5] developed a titrimetric method for the estimation of fluorine using Solochrome Brilliant Blue B.S. (colour index 723) as indicator. WILLARD AND HORTON[2] compared many indicators for use in the titration of fluoride with thorium and came to the conclusion that Purpurin sulphonate and Alizarin Red S are capable of giving reproducible results.

The possibility of using SPADNS, which is the sodium salt of 2-(*p*-sulphophenylazo)-1,8-dihydroxy naphthalene 3,6-disulphonic acid, in the formation of thorium-lake has been recently investigated by the author and, accordingly, methods have been developed for the spectrophotometric determination of microgram amounts of thorium[6] and the titrimetric determination of thorium with fluoride[7]. The following structural formula can be assigned to SPADNS:



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* SPADNS = the sodium salt of 2-(*p*-sulphophenylazo)-1,8-dihydroxynaphthalene-3,6-disulphonic acid.

Since a search of the literature revealed no previous record of a reaction involving thorium and SPADNS, the work embodied in this report was undertaken to develop a new titrimetric method for the estimation of microgram amounts of fluoride ion. The azo dye studied in this work can undergo a ring closure with thorium or zirconium through a hydroxyl group and a co-ordination bond with a nitrogen atom of the azo linkage. The method is based on the fact that SPADNS forms coloured lakes with thorium and zirconium and the colour of the thorium-SPADNS lake being more pronounced than the zirconium lake, the former has been chosen for the investigation. When a solution of sodium fluoride is titrated with thorium nitrate in presence of SPADNS and after an equivalent amount of thorium nitrate has been added, a trace of excess thorium present causes a sharp change in colour of the indicator, the end point being from scarlet-red to blue-violet. The method described for the determination of trace amounts of fluoride ion is rapid and should be of considerable use for analysis of fluoride contents in biological samples. It has the following advantages over the methods in current use:

(1) The colour change is sharp from scarlet-red to blue-violet.
(2) The temperature coefficient of the reagent is low.
(3) The reaction is immediate.

EXPERIMENTAL

Reagents and equipment used

SPADNS, was prepared according to the method outlined by BANERJEE[7] and its 0.02% solution was made in water.

Standard 0.004M thorium nitrate solution (thorium nitrate tetrahydrate, Merck).

Stock solution of 0.1385M pure reagent-grade sodium fluoride was prepared and standardized by the well known method[8], and this was diluted with water in order to have solutions containing different micrograms of fluoride ion per ml.

Buffer (pH 3.09) : 100 ml M sodium acetate solution and 97 ml M HCl were made up to 500 ml with distilled water.

Filter paper, Whatman No. 42, 5.5 cm diameter circles.

Microburette, Nessler glass and white tiles.

Determination of fluoride

Selection of optimum conditions

(*1*) *Concentration of the indicator.* The method involves the matching of colour at the end point with that of a blank. Though the amount of SPADNS does not affect the titre value of a fluoride solution, the ease of matching of colours is greatly influenced by its concentration. Thus, by using 0.5 ml of 0.01% solution of the dye in 50 ml final volume the colour obtained was pale and the change at the equivalence point was difficult to judge. On the other hand, 3 ml of 0.02% solution of the indicator had so much residual red colour that the blue-violet colour of the thorium-lake was masked. In order to obtain the sharpest colour change, 1 ml of a 0.02% solution of SPADNS in 50 ml final volume has been selected.

(*2*) *Effect of pH.* In the absence of a buffer thorium hydroxide begins to precipitate at pH 3.3 and the titration then becomes indefinite, but very reproducible results have been obtained, without going above that pH range by buffering the titrating solutions with sodium acetate-hydrochloric acid buffer. Since the sharpness of the end point is increased in the acid medium, use of sodium acetate-hydrochloric acid buffer ensures that titrations can be safely carried out at pH 3.0.

(3) *Effect of volume of titrating solutions.* Effect of volume of titrating solutions has been studied. To ascertain the effect of dilution upon the end point, titrations were carried out varying the amount of final titrating solutions. It will be obvious from Table I that, without increasing the concentration of SPADNS, dilution can be made upto 100 ml, above which the colour matching becomes difficult.

TABLE I

TITRATION OF FLUORIDE WITH THORIUM NITRATE VARYING THE FINAL VOLUME

Total volume of the solution titrated, ml	10	20	50	100	10	20	50	100
Fluoride ion present, μg	26	26	26	26	52	52	52	52
0.004M $Th(NO_3)_4$ solution required, ml	0.91	0.92	0.92	0.91	1.80	1.81	1.80	1.82

(4) *Effect of adding excess reagent to the blank.* All titrations were carried out by comparing the colour of the titrating solution with that of a blank containing a small amount of thorium and it has been observed that the addition of excess thorium to the blank affects the titration figure. Therefore, during the experiment, 0.05 ml of thorium nitrate solution was always added to the blank. It will be evident from Table II that when the amount of thorium nitrate in the blank is varied, different volumes of 0.004M thorium nitrate solution will be required for titrating 52 μg of fluoride ions.

TABLE II

EFFECT OF EXCESS THORIUM NITRATE ADDED TO THE BLANK

Thorium nitrate added to the blank ml	*Thorium nitrate required by 52 µg of fluoride ml*	*Thorium nitrate required by 52 µg fluoride corrected for blank ml*
0.01	1.79	1.78
0.05	1.85	1.80
0.10	1.94	1.84
0.15	2.04	1.89
0.20	2.12	1.92
0.30	2.45	2.15

Procedure finally adopted

Measured aliquots containing less than 100 μg of fluoride ion were taken in Nessler glasses standing on white tiles for titration. To each glass, 1 ml of the prepared buffer and 1 ml of 0.02% SPADNS were added and the total volume was made up to 50 ml with distilled water. Into each blank standing on a white tile was measured 1.0 ml of the same buffer, 0.05 ml of standard thorium nitrate solution (accurately from a microburette), 1.0 ml of the above indicator, and distilled water to make the total volume equal to that of the sample solution. Then each sample solution was titrated with 0.004M thorium nitrate solution from a microburette until it exactly matched the blank in colour, the end point being from scarlet-red to blue-violet. Results of some microdeterminations carried out in triplicate on known amounts of fluoride are given in Table III.

TABLE III

TITRATION OF FLUORIDE WITH THORIUM NITRATE

Fluoride taken µg	*Fluoride found* µg		
3.2	3.05,	3.4,	3.2
6.5	6.6,	6.4,	6.5
13.0	13.1,	13.05,	13.05
26.0	25.9,	26.1,	26.0
39.0	38.5,	38.8,	39.1
78.0	77.2,	76.9,	77.4
91.0	90.6,	91.0,	90.8

Calibration curve

Since the method outlined above is capable of giving reproducible results, a calibration curve (Fig. I) correlating titration figure and known microgram amount of fluoride has been prepared during the experiment. The same amount of thorium nitrate has been added to the blank tubes during titrations. The results for a typical calibration series are shown in Table IV below:

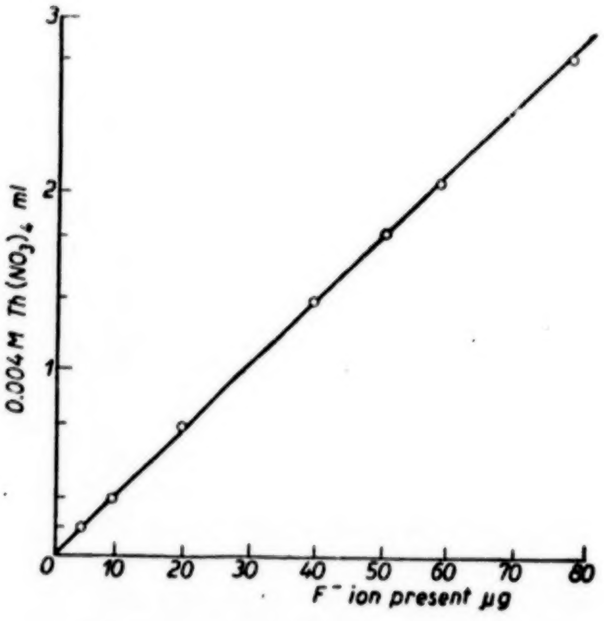

Fig. 1. A typical calibration curve.

TABLE IV

A TYPICAL CALIBRATION SERIES

Fluoride present, µg	5	10	20	40	50	60	78
$0.004M$ $Th(NO_3)_4$ required, ml	0.17	0.36	0.69	1.38	1.71	2.00	2.74

Effect of interfering ions

Effects of various ions on the titration of 52 µg of fluoride ion have been studied and the results have been recorded in Table V. It will be evident from the table that the method is not specific for fluoride ions, as many other ions that complex thorium will behave in the same manner. The method is suitable for the titration of pure solutions of fluoride although with a few exceptions, most other ions will affect the titre value. Accordingly, for the estimation of fluoride associated with interfering substances, it is advisable to separate the fluoride from such substances (*e.g.* SiF_4) by distillation procedure[2] and then the titration can be easily done with thorium-SPADNS lake.

TABLE V

EFFECT OF INTERFERENCES ON TITRATION OF 52 μg OF FLUORIDE

NH_4NO_3 : mg added	0	10	100	500
Titre value, ml	1.81	1.80	1.82	1.88
NaCl : mg added	0	10	100	500
Titre value, ml	1.81	1.85	1.89	*2.05
KCl : mg added	0	10	100	
Titre value, ml	1.81	1.82	1.85	
Na_2CO_3 : mg added	0	1	5	
Titre value, ml	1.81	1.79	**	
Na_2SO_4 : mg added	0	1	10	
Titre value, ml	1.81	1.86	*2.13	
Na_3PO_4 : mg added	0	5	100	
Titre value, ml	1.81	**	**	
Na_2SiO_3 : mg added	0	10	100	
Titre value, ml	1.81	1.82	0.95	
$NaClO_4$: mg added	0	10	100	
Titre value, ml	1.81	1.82	1.82	
$NaBO_2$: mg added	0	1	10	
Titre value, ml	1.81	1.79	**	
Na-acetate : mg added	0	1	10	
Titre value, ml	1.81	1.78	1.25	
Na-tartrate : mg added	0	1	5	
Titre value, ml	1.81	**	**	
Na-citrate : mg present	0	1	2	
Titre value, ml	1.81	Basic colour	Basic colour	

* very poor end point
** decolourised

DISCUSSION

The method is suitable for the determination of microgram amounts of fluoride ions in the range from 1 μg to 100 μg. When the amount of fluoride ion exceeds this value, ThF_4 precipitates out of the titrating solution and affects the matching of colour at the end point. The aliquots taken should therefore be such that the fluoride ion concentration remains within the above limits. Attempts are being made to increase the range by using a suitable protective colloid which will be able to maintain ThF_4 in solution. The principle of the method described here may also be applied to the colorimetric technique and this investigation will be taken up very soon.

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SUMMARY

A rapid titrimetric method has been developed for the determination of microgram amounts of fluoride ion in the range from 1 μg-100 μg in 50 ml final volume. It involves the adjustment of pH, addition of 1 ml of 0.02% SPADNS indicator, dilution to volume and titration with standard 0.004*M* $Th(NO_3)_4$ until the colour obtained matches a blank containing the buffered solution of the indicator with a trace of thorium nitrate solution. Interference by various ions was also studied. The method described for the determination of fluoride ion is very rapid and the colour change at the end point being sharp, the detection of the end point is very easy. The method is applicable to pure solutions of fluorides.

RÉSUMÉ

Une méthode titrimétrique rapide a été développée pour le microdosage de l'ion fluorhydrique pour des teneurs allant de 1 μg à 100 μg/50 ml; elle comprend la fixation du pH, l'addition de 1 ml d'indicateur (SPADNS 0.02%), la dilution et la titration à l'aide d'une solution étalon de $Th(NO_3)_4$ 0.004*M*, jusqu'à ce que la coloration obtenue corresponde à celle obtenue avec essai à blanc : solution tampon de l'indicateur + trace de nitrate de thorium. L'influence de divers ions a été également étudiée. La méthode décrite pour ce dosage est très rapide et le virage étant net, la détermination du point d'équivalence est très facile. Ce procédé est applicable aux solutions pures de fluorures.

ZUSAMMENFASSUNG

Es wurde eine rasche titrimetrische Methode entwickelt für die Mikrobestimmung des Fluorid-Ions bei Gehalten an 1 μg bis 100 μg/50 ml; sie enthält die Fixierung des pH, die Zugabe von 1 ml Indikator (SPADNS 0.02%) die Verdünnung und die Titration mit Hilfe einer Vergleichslösung von $Th(NO_3)_4$ 0.004*M*, bis der Farbumschlag demjenigen des Blindversuches entspricht : Pufferlösung des Indikators + Spuren von Thoriumnitrat. Der Einfluss verschiedener Ionen wurde gleichfalls untersucht. Die für diese Bestimmung beschriebene Methode ist sehr rasch, und da der Umschlag deutlich ist, ist der Gleichgewichtspunkt sehr einfach zu bestimmen. Dieser Prozess kann für reine Fluorid-Lösungen angewendet werden.

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ANALYTICAL APPLICATIONS OF THE PHOTOCHEMICAL ACTION OF LIGHT

II. DETERMINATION OF OXALIC ACID BY PHOTO-OXIDATION IN THE PRESENCE OF FERRIC SALTS

by

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Several methods have been proposed from time to time for the determination of oxalic acid. As early as 1852, MOHR utilized the reaction between pure oxalic acid and pure potassium permanganate in dilute solution for the standardisation of the latter. LUNGE[1], MCBRIDE[2] and BAXTER AND ZANETTI[3] described the conditions under which the reaction could be carried out. According to MCBRIDE, insufficient stirring, high concentration of acid and great dilution of the oxalic acid solution introduced errors. According to GOOCH AND PETERS[4], the presence of hydrochloric acid gave higher results. They found that the hydrochloric acid error could be minimized by adding manganous sulphate. SKRABAL[5] found that manganous salt catalyzed the reaction to such a degree that it was possible to carry out the titration of oxalic acid by potassium permanganate at room temperature. MAPSTONE AND SMITH[6] found that addition of 5 ml of 0.1*M* ferric sulphate solution to 20 ml of 0.1*N* oxalic acid enables the titration to be carried out accurately and quantitatively at 25° C.

ROSENTHALER[7] proposed determining oxalic acid with potassium iodate. The reaction between oxalic acid and excess of potassium iodate proceeds smoothly in hot dilute sulphuric acid medium. After expelling completely all the iodine from the solution, the unreacted potassium iodate was determined. BENRATH AND RULAND[8] studied the kinetics of the reaction of ceric sulphate with various organic acids in sulphuric acid medium. They showed that oxalic acid and ceric sulphate react according to the following equation slowly in the cold and rapidly when heated.

$$H_2C_2O_4 + 2Ce(SO_4)_2 = Ce_2(SO_4)_3 + 2\,CO_2 + H_2SO_4$$

Sulphuric acid and normal sulphate retarded the reaction. WILLARD AND YOUNG[9], FURMAN[10], ATANASIU[11], and STEFANESCU[12] carried out the potentiometric titration of oxalic acid with ceric sulphate at 50° C using iodine monochloride as catalyst. WILLARD AND YOUNG also carried out titrations using the colour of the ceric ion as indicator. Later, WILLARD AND YOUNG[13] carried out the titration of oxalic acid with ceric sulphate at 40° C, using iodine monochloride as catalyst, and *o*-phenanthroline ferrous complex as internal indicator. This method is not quite accurate as the reaction is still somewhat slow because the temperature cannot be increased beyond 40° without the fear of the indicator dissociating. It was for this reason that

SMITH AND GETZ[14] recommended the titration of oxalic acid in perchloric acid solution with ceric perchlorate. It must, however, be noted that ceric perchlorate solutions are not quite stable and require frequent standardization.

ABELMANN[15] determined oxalate by means of its reaction with mercuric nitrate. To a measured volume of the oxalate or oxalic acid solutions, 30 to 40 drops of $5N$ nitric acid and a known excess of $0.1N$ mercuric nitrate solution were added, followed by the addition of 50 ml of saturated potassium nitrate solution. The solution was kept for fifteen minutes and then filtered. The filtrate was titrated with a standard solution of ammonium thiocyanate using ferric alum as indicator.

GOPALA RAO AND MADHUSUDHANA RAO[16] found that ferric sulphate in dilute sulphuric acid solution was rapidly reduced to the ferrous state when exposed to sunlight in the presence of oxalic acid. The ferrous salt thus formed was determined by titration with a standard solution of sodium vanadate. This rapid photoreaction has thus been utilized analytically for the determination of ferric salts.

In the work presented here, we have investigated the application of the photochemical reaction between oxalic acid and ferric sulphate to the determination of oxalic acid. A measured volume of oxalate solution was mixed with an excess of ferric alum solution, acidified with sulphuric acid, and exposed to sunlight or artificial light. After the reaction was completed, the ferrous iron formed was determined using a standard solution of sodium vanadate. This gave a measure of the oxalic acid present.

EXPERIMENTAL

Reagents

1. A decinormal solution of ferric alum was prepared using Merck's "pro analysi" grade ferric alum.
2. A $0.04492N$ sodium oxalate solution was prepared from Merck's "pro analysi" grade sodium oxalate.
3. A standard solution of sodium vanadate was prepared using the A.R. ammonium vanadate manufactured by the British Drug House Ltd. This solution was standardized against a standard solution of Mohr's salt.

TABLE I

THE REACTION MIXTURE CONSISTED OF 10 ml OF $0.04492N$ OXALIC ACID SOLUTION + 10 ml OF $0.1N$ FERRIC ALUM SOLUTION + 10 ml OF $4N$ SULPHURIC ACID DILUTED TO 50 ml IN A QUARTZ BEAKER

Amount of oxalic acid = 0.4492 mg equivalents

Period of exposure to sunlight	*Amount of oxalic acid found*
8 minutes	0.4352 mg equivs.
15 ,,	0.4492 ,,
30 ,,	0.4492 ,,

From the above, it is seen that all the oxalic acid was completely oxidized by the ferric alum, when exposed to bright sunlight for only fifteen minutes.

The following experiments were conducted with varying amounts of oxalic acid. In each case, care was taken to see that an excess of ferric alum was added. The ratio of $Fe : C_2O_4^{=}$ was invariably maintained at 4 : 1 or higher.

TABLE II

Time of exposure to sunlight = 20 minutes

Amount of oxalic acid taken in mg equivs.	*Amount of oxalic acid found in mg equivs.*
0.2246	0.2244
0.4492	0.4491
0.6738	0.6729
0.8984	0.8972

The results show that oxalic acid can be determined accurately by the photochemical method now proposed. It was also found that varying the overall concentration of sulphuric acid within the limits of 0.2 to 0.8M did not affect the rate of photo-oxidation of oxalic acid.

Determination of oxalic acid in the presence of formic acid

Although formic acid by itself does not react with potassium permanganate in acid medium, we found that it interfered in the determination of oxalic acid by permanganate in the usual way. In the following experiments, varying quantities of sodium formate were added to 10 ml of oxalic acid solution, which was then acidified with sulphuric acid, diluted to 100 ml and titrated with standard potassium permanganate at 60-80° C.

TABLE III

Amount of oxalic acid taken	*Sodium formate added*	*Amount of permanganate consumed*
0.4550 mg equivs.	nil	0.4550 mg equivs.
0.4550 ,,	0.2118 mg equivs.	0.4576 ,,
0.4550 ,,	0.3117 ,,	0.4603 ,,
0.4550 ,,	0.5295 ,,	0.4629 ,,
0.4550 ,,	0.8472 ,,	0.4686 ,,
0.4550 ,,	0.9531 ,,	0.4686 ,,
0.4550 ,,	1.0590 ,,	0.4686 ,,

From the above, it is obvious that oxalic acid cannot be estimated with potassium permanganate in the presence of formic acid.

Our experiments have shown that formic acid does not interact with ferric sulphate in sunlight. The following experiments were conducted to study whether formic acid interferes in the photochemical method of determination of oxalic acid.

TABLE IV

Reaction mixtures consisting of 10 ml of 0.0455N oxalic acid solution + 10 ml of 0.1N ferric alum solution + X ml of 0.2004N sodium formate solution + 15 ml of 4N sulphuric acid were diluted to 60 ml and exposed in a quartz beaker for 15 minutes.

Amount of oxalic acid taken in mg equivs.	*Amount of formic acid added in mg equivs.*	*Amount of oxalic acid found in equivs.*
0.4550	0.4008	0.4553
0.4550	0.8016	0.4554
0.4550	1.2024	0.4553
0.4550	1.6032	0.4550
0.4550	2.000	0.4550

The results show that oxalic acid can be determined accurately even in the presence of a large excess of formic acid by the photochemical method now proposed. It has been found that formic acid does not interact with ferric chloride even during a prolonged exposure of 60 minutes.

Experiments have also been conducted on the determination of oxalic acid by photochemical oxidation in the presence of ferric sulphate using light from a 1000 watt tungsten filament lamp or in the ultra-violet light from a quartz mercury vapour lamp. With the former source, oxidation was complete for an exposure of about three hours, and with the latter about six hours.

SUMMARY

A new method has been developed for the determination of oxalic acid. This depends upon the photochemical oxidation of oxalic acid in the presence of ferric sulphate.

The method involves exposing a measured volume of oxalic acid solution, with an excess of ferric alum and some sulphuric acid, tosunlight in a quartz or pyrex beaker for 15 to 30 minutes. The progress of the reaction is indicated by the disappearance of the yellow colour of the ferric-oxalate complex from the solution. After completion of the reaction, the ferrous salt formed is determined using standard sodium vanadate and either diphenylbenzidine or diphenylamine sulphonate as internal indicator in the presence of sufficient phosphoric acid.

Formic acid does not interfere in the photochemical method of determination.

RÉSUMÉ

Une nouvelle méthode a été développée pour le dosage de l'acide oxalique. Elle est basée sur l'oxydation photochimique de l'acide oxalique par le sulfate de fer(III). La méthode consiste à exposer à la lumière solaire un volume déterminé d'une solution d'acide oxalique, en présence d'un excès d'alun ferrique et d'acide sulfurique, (dans un bécher de quartz ou de pyrex) pendant 15 à 30 minutes, jusqu'à disparition de la coloration jaune du complexe fer(III) - oxalate. Le fer(II) formé est ensuite dosé par une solution étalon de vanadate de sodium, en présence de diphénylbenzidine ou de diphénylamine sulfonate comme indicateur et d'acide phosphorique. L'acide formique ne gêne pas.

ZUSAMMENFASSUNG

Es wurde eine neue Methode entwickelt, um Oxalsäure zu bestimmen. Sie basiert auf der photochemischen Oxydation der Oxalsäure mit Eisen(III)-sulfat. Die Methode besteht darin, eine gemessene Menge Oxalsäure-Lösung in Gegenwart eines Eisenalaun-Überschusses und Schwefelsäure (in einem Quarz- oder Pyrex-Becherglas) während 15-30 Minuten dem Sonnenlicht auszusetzen, bis zum Verschwinden der Gelbfärbung des Eisen(III)-Oxalat-Komplexes. Das gebildete Eisen(II) wird darauf mit einer Natriumvanadat-Vergleichslösung bestimmt, in Gegenwart von Diphenylbenzidin oder Diphenylaminsulfonat als Indikator und Phosphorsäure. Die Ameisensäure stört nicht.

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CERATE OXIDIMETRY

III. OXIDATION OF GLYCEROL, GLYCOL AND OTHER ORGANIC COMPOUNDS

by

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The classical acetin method[1] for the estimation of glycerol is of limited applicability. A large number of methods based on the oxidation of glycerol by potassium dichromate, permanganate[2,3,4,5,6] and periodate[7] have been described. A summary of the oxidimetric methods employed has been recently given by HARTMAN[8] and is omitted here.

Oxidation of glycerol by ceric sulphate was attempted by CATHILL AND ATKINS[9] who assumed that glycerol is oxidized quantitatively to tartronic acid under specific conditions.

$$C_3H_8O_3 + 4[O] \rightarrow C_3H_4O_5 + 2H_2O$$

However, the same eight equivalents of oxygen would be required even if the oxidation of glycerol proceeded to formic acid as shown below:

$$C_3H_8O_3 + 4[O] \rightarrow 3H\,COOH + 2H_2O$$

It has already been reported that formic acid is the final oxidation product in the case of a number of organic compounds. SMITH AND DUKE[10] have shown that glycerol on treatment with perchlorato-cerate is oxidized to formic acid by the latter reaction. In view of the above, it seemed improbable that the oxidation of glycerol by sulphato-cerate proceeded via tartronic acid. To test this, the oxidation of tartronic acid itself by ceric sulphate was studied. It has been shown (Table II) that tartronic acid is easily oxidized quantitatively by ceric sulphate and hence it can be concluded that tartronic acid could not be the final end product in the oxidation of glycerol with ceric sulphate.

In recent communications[11,12], the authors have shown that formic acid can be oxidized completely to carbon-dioxide and water with ceric sulphate in the presence of large concentrations of sulphuric acid. The ceric sulphate sample employed was a Schuchardt product. A number of workers[13,14,15] have repeatedly reported that the rare-earths impurities generally present do not affect the oxidizing power of ceric sulphate and in view of the above, the sample, as stated[11,12] was employed without further purification. If, as assumed above, formic acid were the end product in the oxidation of glycerol with ceric sulphate, it should be possible to oxidize it further by the above procedure. However, it was found that with carefully purified ceric sulphate, the oxidation did not proceed beyond formic acid stage although with the Schuchardt sample, the oxidation of glycerol could be completed to carbon dioxide and water.

In view of the above, the oxidation of formic acid itself was repeated and it was confirmed that the oxidation of formic acid by pure ceric sulphate was negligible. Hence, it was concluded that some impurity present in the ceric sulphate could catalyse the oxidation of formic acid to carbon dioxide.

An extensive search revealed that almost all rare-earth elements, iron, manganese, silver, osmium *etc.* do not exert any appreciable catalytic influence on the above reaction. Finally it has been found that chromium has a marked catalytic activity and in the presence of a drop of 1% chromium sulphate solution for every 5 ml of ceric sulphate solution employed, the oxidation of formic acid could be completed exactly as described in the earlier publications[11,12]. The presence of chromium in the Schuchardt sample was confirmed by the diphenyl carbazide test. Before proceeding further with glycerol, it was therefore, considered important to repeat the oxidation of various organic compounds. In the following table are given the results obtained when one drop of 1% chromium sulphate is added to the pure ceric sulphate solution under the conditions described in the earlier publications[11,12].

TABLE I

Name of the acid	*Found* g	*Present* g
Formic	0.00684	0.00685
Malic	0.00447	0.00447
Malonic	0.00433	0.00433
Glycolic	0.00469	0.00468
Tartaric	0.00644	0.00643
Fumaric	0.00389	0.00387
Maleic	0.00237	0.00235
Salicylic	0.00255	0.00256
Benzoic	0.00333	0.00332
Phthalic	0.00247	0.00247

The oxidation of glycerol and also glycol with ceric sulphate has been studied in the present investigation (Tables III, V). It has been found that both are quantitatively oxidized to formic acid only.

Further it has been shown that both can be oxidized completely to carbon dioxide and water by ceric sulphate in the presence of a high concentration of sulphuric acid and chromium as catalyst (Tables IV, VI). The possibility of quantitatively oxidizing glycol and glycerol to two definite stages under different conditions with ceric sulphate has been utilized in a method for the estimation of glycol and glycerol when present together in a mixture (Table VII).

EXPERIMENTAL

Materials: Ceric ammonium nitrate employed was a B.D.H. Analar product and solutions of the salt in sulphuric acid were directly prepared. Glycerol was a B.D.H. Analar sample. Glycol was a pure Merck product.

Standardization of ceric sulphate was carried as described earlier[11,12]. 0.1275*N* ceric sulphate solution employed in the investigation was in 2*N* sulphuric acid.

Tartronic acid: The solution of tartronic acid (Purkis and Williams' product) was prepared by dissolving a weighed amount in water and was then standardized by oxidation with potassium dichromate. The sample showed a purity of 98.14%.

5 ml of ceric sulphate and 2 ml of tartronic acid solution were mixed and refluxed for varying intervals of time. The remaining excess of ceric sulphate was determined as described earlier[11,12] and from the amount of ceric sulphate consumed, the amount of tartronic acid was calculated assuming that it is completely oxidized to carbon dioxide and water.

TABLE II

0.1275N $Ce(SO_4)_2$ ml	Tartronic acid ml	Refluxing time min	$Ce(SO_4)_2$ consumed ml	Tartronic acid Found g	Tartronic acid Present g
5	2	5	2.78	0.00708	0.00793
5	2	10	3.10	0.00790	,,
5	2	15	3.11	0.00793	,,
5	2	120	3.11	0.00793	,,

Glycerol : The glycerol solution was standardized by oxidation with potassium dichromate. Known volumes of the glycerol solution were added to measured volumes (excess) of ceric sulphate. The solution was refluxed for a definite time and then the excess ceric sulphate was determined.

TABLE III

0.1275N $Ce(SO_4)_2$ ml	Glycerol solution ml	Refluxing time min	$Ce(SO_4)_2$ consumed ml	Equivalent of O_2 used
5	2	5	2.775	7.68
5	2	10	2.84	7.86
5	2	15	2.89	8.00
5	2	60	2.89	8.00
5	2	120	2.89	8.00

In Table IV are given the results indicating complete oxidation of glycerol to carbon dioxide and water in the presence of chromium as catalyst. The mixture of glycerol and ceric sulphate was first refluxed for 10-20 minutes and then concentrated sulphuric acid and a drop of 1% chromium sulphate solution were added and the refluxing continued after, which the excess ceric sulphate was titrated against ferrous sulphate.

TABLE IV

Glycerol solution ml	0.1275N $Ce(SO_4)_2$ ml	Time of initial refluxing min	Conc. H_2SO_4 ml	Time of final refluxing min	$Ce(SO_4)_2$ consumed ml	Glycerol Found g	Glycerol Present g
2	10	15	25	50	5.06	0.00429	0.00430
2	10	20	12	70	5.055	0.00428	,,
2	10	10	12	75	5.06	0.00429	,,
2	10	15	12	75	5.06	0.00429	,,

Glycol : The glycol solution was standardized by oxidation with potassium dichromate[16]. Known volumes of the glycol solution were treated with ceric sulphate as described in the case of glycerol.

TABLE V

0.1275N $Ce(SO_4)_2$ ml	Glycol solution ml	Refluxing time min	$Ce(SO_4)_2$ consumed ml	Equivalents of O_2 used
5	2	15	2.71	5.07
5	2	20	3.07	5.75
5	2	25	3.23	6.00
5	2	30	3.235	6.03
5	2	60	3.23	6.00
5	2	120	3.23	6.00
5	2	240	3.235	6.03

The oxidation of glycol, like glycerol, can also be completed to carbon dioxide and water. Table VI shows the results obtained when the oxidation of glycol is catalysed by chromium in the presence of sulphuric acid.

TABLE VI

Glycol solution	*0.1275N $Ce(SO_4)_2$*	*Time of initial refluxing*	*Conc. H_2SO_4*	*Time of final refluxing*	*$Ce(SO_4)_2$ consumed*	*Glycol*	
						Found	*Presen*
ml	*ml*	*min*	*ml*	*min*	*ml*	*g*	*g*
2	10	30	12	75	5.38	0.00323	0.00324
2	10	20	15	70	5.38	0.00323	,,
2	10	—	10	60	5.38	0.00323	,,
2	10	—	15	60	5.385	0.00324	,,

MIXTURES OF GLYCOL AND GLYCEROL

The data in the Tables (III and V) show that both glycol and glycerol are quantitatively oxidized to formic acid by ceric sulphate in less than half an hour and further refluxing does not effect any further oxidation. However, according to the data in the Tables (IV and VI) both glycol and glycerol can be quantitatively oxidized to carbon dioxide and water under the conditions described. By utilizing the above, it is possible to develop a method for the estimation of glycol and glycerol when present in a mixture.

Different volumes of glycol and glycerol solutions were mixed together and the total volume made up to 50 ml. 2 ml portions of these were taken and treated in duplicate against ceric sulphate solution. To both the portions, excess of ceric sulphate was added and the mixtures refluxed for 30 minutes, after which ceric sulphate was determined in one of the samples. To the second portion, one drop of chromium sulphate (1%) and concentrated sulphuric acid were added and refluxing continued. The remaining excess of ceric sulphate was then determined as usual. Table VII gives the results obtained. In the last two columns are shown the volumes of the glycerol and glycol solution found and within brackets are given the corresponding volumes actually present in the mixture.

TABLE VII

2 ml of mixture no.	*0.1275N $Ce(SO_4)_2$ ml*	*Time of initial refluxing min*	*Conc. H_2SO_4 ml*	*Time of refluxing min*	*$Ce(SO_4)_2$ consumed ml*	*Vol. of glycol present ml*	*Vol. of glycerol present ml*
1	5	30	—	—	1.999	—	—
	5	30	7	70	3.447	10.0(10.0)	20.0(20.0)
2	5	30	—	—	1.938	—	—
	5	30	7	70	3.287	20.14(20.0)	9.88(10.0)
3	5	30	—	—	2.03	—	—
	5	30	7	70	3.53	4.48(5.0)	25.2(25.0)
4	5	30	—	—	1.907	—	—
	5	30	7	70	3.207	25.1(25.0)	5.0(5.0)
5	5	30	—	—	2.625	—	—
	10	30	12	70	4.489	20.1(20.0)	19.87(20.0)

SUMMARY

1. Oxidation of tartronic acid has been studied and it has been shown that the oxidation of glycerol by ceric sulphate does not proceed via this acid as was presumed by earlier workers.

2. It has been shown that the oxidation of formic acid by pure ceric sulphate is negligible, but using chromium sulphate as catalyst, formic acid can be quantitatively oxidized.

3. Oxidation of glycol and glycerol can be carried out quantitatively either to the formic acid stage or completely to carbon dioxide and water. A combination of the above provides a method for the estimation of the two compounds when present together in a mixture.

RÉSUMÉ

1. L'oxydation de l'acide tartronique a été étudiée. Il est démontré que l'oxydation du glycérol par le sulfate de cérium(IV) ne se fait pas par l'intermédiaire de cet acide comme l'ont supposé certains chercheurs.

2. Il est démontré que l'oxydation de l'acide formique par le sulfate de cérium(IV) est négligeable, mais en présence de sulfate de chrome comme catalyseur, l'acide formique peut être oxydé quantitativement.

3. L'oxydation du glycol et du glycérol peut se faire quantitativement soit en acide formique, soit complètement en anhydride carbonique et eau. Une combinaison de ces deux oxydations permet le dosage de ces deux composés lorsqu'ils se trouvent simultanément dans le même mélange.

ZUSAMMENFASSUNG

1. Die Oxydation der Tartronsäure wurde untersucht. Es wird gezeigt, dass die Oxydation des Glyzerols mittels Cerium(IV)sulfat sich nicht über diese Säure vollzieht, wie gewisse Autoren angenommen haben.

2. Es wird gezeigt, dass die Oxydation der Ameisensäure mittels Cerium(IV)sulfat zu vernachlässigen ist, aber in Gegenwart von Chromsulfat als Katalysator, kann die Ameisensäure quantitativ oxydiert werden.

3. Glykol und Glyzerol können quantitativ zu Ameisensäure oder vollständig zu Kohlendioxyd und Wasser oxydiert werden. Eine Kombination dieser beiden Oxydationen erlaubt eine Bestimmung dieser beiden Verbindungen, wenn sie sich gleichzeitig in derselben Mischung befinden.

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ESTIMATION OF SILICA

by

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The method for the determination of silica in silicate rock by the classical procedure does not give highly accurate results, as is evident from the work of GUTHRIE AND MILLER[1]. A simpler and more direct method for the estimation of silica being desirable, attempts have been made by many investigators[2,3,4] to precipitate silica as a sparingly soluble salt of silicomolybdic acid with organic bases.

MILLER AND CHALMERS[5] proposed the use of 2:4-dimethylquinoline as the precipitant and silicomolybdic anhydride as the weighing form in preference to the other methods.

With 5,6-benzoquinaldine[6] and 8-hydroxyquinaldine[7] as the organic bases, we found that the sparingly soluble salts formed by these bases with silicomolybdic acid are quite stable and non-hygroscopic and hence can be weighed directly after drying at 110° C. Even at 150° C, the loss in weight is quite negligible and at 550° C, they decompose completely to silicomolybdic anhydride. The compositions of the precipitates subsequent to drying at 110-150° C are assumed to be $H_4SiO_4 \cdot 12MoO_3 \cdot 4C_{14}H_{11}N$ and $H_4SiO_4 \cdot 12MoO_3 \cdot 4C_{10}H_9ON$ respectively.

During ignition to the anhydride, free access of air is essential to prevent the reduction of molybdenum.

EXPERIMENTAL

Reagents

Reagent grade chemicals are always used.

Sodium silicate solution. Different solutions are prepared by fusing 97% pure ignited quartz with sodium carbonate and dissolving in water.

5,6-Benzoquinaldine. A 2% solution of the base (m.p. 81-82° C) in 100 ml of 0.25*N* hydrochloric acid is prepared.

As the hydrochloride of the base crystallizes out at room temperature, the mixture should be heated on a waterbath to dissolve the hydrochloride before use.

8-Hydroxyquinaldine. A 1% solution of the base in 0.25*N* hydrochloric acid is used.

Analytical procedure

(I) *With 5,6-benzoquinaldine.* A sample containing about 3-10 mg of silica is fused with 100 mg of sodium carbonate in a platinum crucible for half-an-hour and dissolved after cooling in 5 ml of warm water. This is then added with constant stirring to a mixture of 6-8 ml of ammonium molybdate (10% w/v) and 1.5 ml of 6.0*N* hydrochloric acid. The crucible is rinsed with water and the washings are added to the main solution, the total volume of which is made up to 50 ml.

The solution is then heated on a waterbath for about five minutes and to it are added successively 6 ml of 6.0*N* hydrochloric acid and 6-8 ml of the 5,6-benzoquinaldine solution with vigorous stirring. After dilution to 100 ml, the solution is again heated on a waterbath for about ten minutes and the clear supernatant liquid is filtered through a weighed sintered porcelain crucible. The precipitate is washed by decantation three times with hot 1% hydrochloric acid and then, since the molybdate of the base is less soluble in water and decomposes with the liberation of the free base in ammoniacal solution, 100 ml of water are added to the precipitate in the beaker and the contents rendered faintly ammoniacal. Here care should be taken to see that the temperature of the solution does not rise above 30° C. A white emulsion of the free base is formed at the top, while yellow salt of 5,6-benzoquinaldine silicomolybdate settles at the bottom. The solution is filtered again by decantation through the crucible and washed six times by decantation with cold 1% ammonia solution, thrice with water and thrice with cold 1% hydrochloric acid solution. The precipitate is transferred to the crucible with hot 1% hydrochloric acid, washed with it four times and washed with hot water till free from acid. It is then dried at 110° C and weighed. It can also be dried at 150° C. Alternatively, it can be ignited at 550° C in a furnace with free access of air to silicomolybdic anhydride and weighed.

(II) *With 8-hydroxyquinaldine.* As in the previous procedure, a 1-3 mg sample of silica is fused with 100 mg of sodium carbonate and the cooled melt is disintegrated in 5 ml of warm water. The solution thus prepared is added with stirring to a mixture of 5 ml of ammonium molybdate solution (10% w/v) and 1.2 ml of 6.0*N* hydrochloric acid. The crucible is washed with water and the washings are added to the main solution whose volume is thus made up to about 75 ml. This solution is then warmed at 60° C for ten minutes and to it are added first 25 ml of 8-hydroxyquinaldine and then 20 ml of hydrochloric acid (10% v/v). This is again left on the waterbath for about fifteen minutes, then cooled to room temperature, filtered through a weighed sintered porcelain crucible, washed four or five times with cold water, dried at 110° C or 150° C and weighed or ignited at 550° C and then weighed as the silicomolybdic anhydride.

RESULTS

TABLE I

PROCEDURE I

Silica taken	*Dried at 110° C*		*Dried at 150° C*		*Ignited at 550° C*	
	Salt	*Silica found*	*Salt*	*Silica found*	*Anhydride*	*Silica found*
mg	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*
8.3	355.0	8.2	354.6	8.2	245.2	8.24
3.8	160.6	3.71	160.4	3.7	113.2	3.8

TABLE II

PROCEDURE II

Silica taken	*Dried at 110° C*		*Dried at 150° C*		*Ignited at 550° C*	
	Salt	*Silica found*	*Salt*	*Silica found*	*Anhydride*	*Silica found*
mg	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*
1.020	42.0	1.02	41.4	1.01	30.8	1.03
2.5	102.0	2.49	101.7	2.48	75.5	2.54

Further work in this field is in progress.

SUMMARY

5,6-Benzoquinaldine and 8-hydroxyquinaldine have been used as organic bases for the quantitative precipitation of silica as silicomolybdic salts of the bases under suitable conditions of

acidity. The salts, being stable and non-hygroscopic, may be directly weighed after drying at 110-150° C or alternatively may be ignited at 550° C with free access of air to silicomolybdic anhydride.

RÉSUMÉ

La 5.6-benzoquinaldine et la 8-hydroxyquinaldine ont été utilisées pour la précipitation quantitative du silicium sous forme de sels de l'acide silicomolybdique, dans des conditions déterminées de pH. Les sels obtenus étant stables et non hygroscopiques, ils peuvent être pesés directement après séchage à 110-150° C; on peut également les calciner à 550° C à l'air libre.

ZUSAMMENFASSUNG

Das 5.6-Benzochinaldin und das 8-Hydroxychinaldin wurden zur quantitativen Ausfällung des Siliziums in Form von Salzen der Silikomolybdänsäure, unter bestimmten pH-Bedingungen, verwendet. Die erhaltenen Salze sind stabil und nicht hygroskopisch und können direkt nach der Trocknung bei 110-150° C gewogen werden; man kann sie ebenfalls bei 550° C an der Luft kalzinieren.

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SUR LA STABILITÉ THERMIQUE DES ÉTALONS ANALYTIQUES. II *

par

CLÉMENT DUVAL

avec la collaboration technique de Mlles COLETTE WADIER ET YVETTE SERVIGNE

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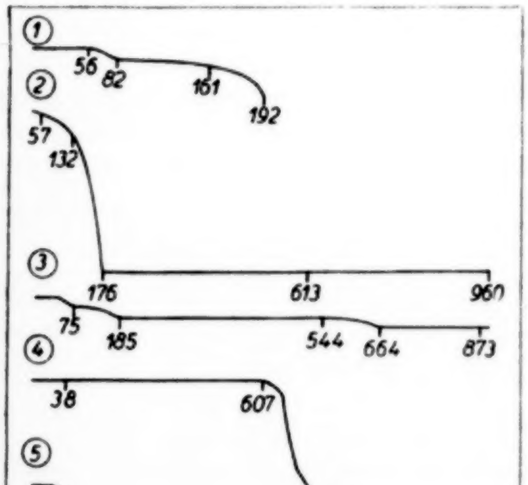
Dans cette deuxième série, nous présentons une nouvelle liste de produits organiques et minéraux rassemblés tout simplement dans l'ordre chronologique et pour lesquels nous avions tracé précédemment les courbes de thermolyse et enregistré les spectres d'absorption infrarouges pour certains de nos correspondants.

Les corps étudiés sont: l'acide citrique, l'acétate d'ammonium, le carbonate de baryum, l'hydroxyde de baryum, le nitrate de baryum, l'acide borique, le chlorure d'ammonium, l'anhydride arsénieux, le sulfate de cadmium, le phosphate diammonique, l'alun de potassium et le tungstate de sodium.



Courbes de thermolyse. (1) Acide citrique. (2) Acétate d'ammonium. (3) Hydroxyde de baryum. (4) Nitrate de baryum. (5) Acide borique. (6) Chlorure d'ammonium.

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Acide citrique

Le produit commercial utilisé a été soumis à une recristallisation dans l'eau et nous a donné la courbe 1. Il est monohydraté avec la formule $C_6H_8O_7.H_2O = 210.14$. Il conserve l'eau de cristallisation jusqu'à 56° avec une vitesse de chauffage de 150° par heure et un poids de substance de 138.2 mg. De cette température à 82°, l'eau s'échappe d'une manière régulière et l'on peut garder l'acide anhydre entre 82 et 131°. La décomposition commence alors très lentement jusqu'à 161°; elle s'accélère ensuite et la perte de poids atteint 61 mg à 192°, terme de notre expérience. Pour la confection des tampons, on fera donc recristalliser l'acide et on le séchera au-dessous de 56°.

Voici d'ailleurs le spectre d'absorption infrarouge réalisé entre 666 et 1600 cm^{-1}, sur poudre humectée d'un peu de vaseline et enregistré avec l'appareil Perkin-Elmer 12C, équipé avec un prisme de sel gemme: 785F, 824f, 888f (large), 903tf, 936f, 1018F, 1055f, 1075f, 1108F, 1169aF, 1210F, 1232f, 1255aF, 1287aF, 1313aF.

Acétate d'ammonium

Ce corps de formule $NH_4CO_2\text{-}CH_3 = 77.08$ est comme l'on sait, très utilisé comme tampon et comme il se montre très déliquescent, il est difficile à peser. On pouvait donc se trouver en droit d'attendre le secours de la thermogravimétrie pour faciliter l'opération. La courbe 2 relative à 223.6 mg de produit chauffé à la vitesse de 300° par heure, indique un départ d'eau dès la température ordinaire ne s'achevant qu'à 176°. On ne peut donc pas faire la distinction entre l'eau de mouillage et l'eau chimiquement liée dont la perte conduit successivement à l'acétamide et à l'acétonitrile. Ces deux corps sont trop volatils pour donner naissance à des paliers de poids constant; le creuset est donc vidé et se maintient avec le même poids jusqu'à 865° et même au-delà. En vue de faire une liqueur titrée, il faut donc s'astreindre à effectuer un dosage d'ammoniac sur la solution préparée.

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* Pour le premier mémoire de cette série, voir *Anal. Chim. Acta*, 13 (1955) 32.

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Le spectre infrarouge dans la même région que la précédente, est beaucoup plus simple puisqu'il n'y a que deux atomes de carbone et pas de fonction alcool tertiaire. Les cristaux choisis étaient suffisamment secs pour ne pas altérer les lamelles de sel gemme servant à confectionner les cuves. Nous avons mesuré les bandes suivantes: 894tf, 925TF, 1010F, 1051F, 1150f, 1163f, 1238f.

Carbonate de baryum

Le carbonate de baryum $BaCO_3$ = 197.37, extrait d'un flacon commercial a été chauffé de 20 à 975°; il ne change pas de poids. La courbe de thermolyse, non reproduite, est donc une horizontale. Ce résultat diffère bien entendu de celui que nous avons annoncé précédemment[1], attendu qu'il s'agissait alors de précipités servant à doser le baryum et retenant l'eau énergiquement. Rappelons que dans ce cas, la déshydratation est pratiquement complète à 400°.

Le carbonate de baryum a fourni un spectre infrarouge très caractéristique du groupement CO_3, avec les bandes suivantes: 695F, 856TF, 1058aF.

Hydroxyde de baryum

Nous nous sommes adressés à plusieurs échantillons commerciaux d'hydroxyde de baryum, à un produit Kalbaum sec, à un produit OSI hydraté et à un produit rehydraté par nous à partir du produit sec.

Le produit sec avait repris de l'humidité, de toute évidence, un peu plus d'une molécule d'eau. Il commence à se déshydrater dès la température ordinaire et entre 75 et 134°, la courbe de thermolyse présente un palier horizontal qui s'accorde presque avec $Ba(OH)_2.1H_2O$; on a déjà signalé avant nous $Ba(OH)_2.0.97\ H_2O$. Le produit anhydre $Ba(OH)_2$ s'obtient de 166 à 180° par chauffage linéairement croissant à raison de 300° par heure et pour un poids initial de 232 mg. La courbe se maintient horizontale jusqu'à 544° et là commence un double phénomène: la déshydratation de l'hydroxyde et l'oxydation de l'oxyde formé. Entre 664 et 772°, la moitié de l'oxygène du peroxyde se dégage très lentement; au-dessus, on obtient le palier horizontal de l'oxyde BaO exempt de carbonate comme le montre le spectre infrarouge.

A partir du produit OSI, appelé hydraté, on remarque que le corps de départ ne contient pas 8 H_2O, mais environ 5.8 H_2O. Nous n'observons pas le petit palier précédent pour le monohydrate, mais une simple inflexion dans la courbe. La baryte s'obtient au-dessus de 728°. On voit que par ces deux cas, il est impossible de considérer le produit tel quel du flacon et que les étiquettes des marchands sont souvent trompeuses; il est nécessaire de faire une déshydratation contrôlée pour partir d'une liqueur titrée exacte.

Un produit rehydraté à 15° à l'abri du gaz carbonique, à partir du produit sec, nous a donné au départ $Ba(OH)_2.4.5H_2O$.

Le spectre infrarouge entre 6 et 15 μ, sur la baryte sèche non carbonatée, nous fournit une bande large et faible à 774 et une autre à 974-986 cm^{-1}. Quand le produit est légèrement carbonaté, on peut déceler vers 851-856 cm^{-1}, la bande relative au groupement CO_3.

Nitrate de baryum

Le nitrate de baryum extrait de divers flacons est sec et anhydre. Son poids se conserve, en chauffage linéaire de 300° par heure jusque vers 592-600°. Pour six corps chauffés, les températures trouvées restent comprises entre 590° et 605°, c'est-à-dire, au voisinage du point de fusion. La décomposition est alors très brutale et à 980°, un poids constant s'obtient pour l'oxyde BaO. Le produit final de ces dissociations est considéré par certains comme un mélange $BaO + BaO_2$, mais notre calcul nous donne 148 et 149 comme poids moléculaire moyen pour le résidu, c'est à dire un nombre compris entre BaO et Ba_2O. Une étude physique (rayons X) se montre nécessaire pour élucider la structure de ce mélange.

Dans le domaine infrarouge habituel, le nitrate de baryum est caractérisé par deux fortes bandes à 816° et 1352 cm^{-1}.

Acide borique

Nous avons déjà étudié[2] la courbe de thermolyse de cet acide et nous rappelons qu'il n'est stable que jusqu'à 55°. D'ailleurs, la déshydratation est complètement achevée à 443°, après un court palier

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relatif à l'acide métaborique. Les conclusions de cette étude sont donc au nombre de deux: (a) on peut peser l'acide borique retiré d'un flacon ayant été plusieurs fois ouvert; la courbe part horizontalement; le produit est bien sec; (b) si l'on veut peser de l'anhydride, il sera bon de maintenir cet acide au-dessus de 443°. Rappelons encore (question souvent posée) que la courbe de thermolyse ne prévoit pas l'apparition de l'acide tétraborique (courbe 5).

Le spectre infrarouge, dans la région habituelle, se fait remarquer par deux bandes fortes: 882 et 1188 cm^{-1}. Cette dernière (c'est-à-dire 8.4 μ) est tout à fait caractéristique et peut servir à identifier l'ion BO_3.

Chlorure d'ammonium

Nous avons déjà enregistré une courbe relative au chlorure d'ammonium préalablement humidifié[3]. Lorsqu'on prélève du chlorure d'ammonium d'un flacon neuf ou usagé, on constate qu'il n'y a pas de perte de poids depuis la température ordinaire jusqu'à 173°. Alors commence une sublimation assez rapide qui peut atteindre 323 mg à 340°, relativement à un poids initial de 523 mg (courbe 6).

Le spectre infrarouge présente une série de bandes faibles pour 844, 851, 888, 916, 935, 969 cm^{-1}, une bande assez forte pour 1074 cm^{-1}, trois bandes faibles pour 1150, 1162 et 1305 cm^{-1}.

Anhydride arsénieux

L'anhydride arsénieux retiré d'un flacon neuf donne une courbe de thermolyse qui se maintient horizontalement jusqu'à 200°. La sublimation commence alors très brutalement pour s'achever à 534° quand le creuset est vide, avec inflexion très marquée entre 350 et 450° (courbe 7). On peut donc faire des liqueurs titrées en pesant directement le produit.

Le spectre infrarouge présente une bande très forte pour 806 cm^{-1}, pouvant s'accommoder avec la présence de groupements AsO_4 avec atome d'oxygène mis en commun, quatre bandes faibles pour 842, 916, 931 et 1035 cm^{-1}, une bande assez forte à 1053 cm^{-1}.

Sulfate de cadmium

Nous avions déjà donné[4] la courbe de thermolyse du sulfate de formule $CdSO_4.8/3H_2O$ qui doit se préparer tout spécialement, mais le produit retiré des flacons commerciaux a probablement été cristallisé entre 80 et 100° et correspond assez généralement au monohydrate que l'on peut d'ailleurs peser tel qu'il sort du flacon. En effet, d'après notre courbe de thermolyse (courbe 8), il ne perd pas de poids avant 160°; la déshydratation est achevée en chauffage continu de 300° par heure, à 261°; au-dessus de cette température s'étend le palier horizontal du sulfate neutre anhydre.

Le monohydrate fournit les bandes d'absorption infrarouge suivantes: 824f, 893F, 993aF, 1074F, 1174aF cm^{-1}.

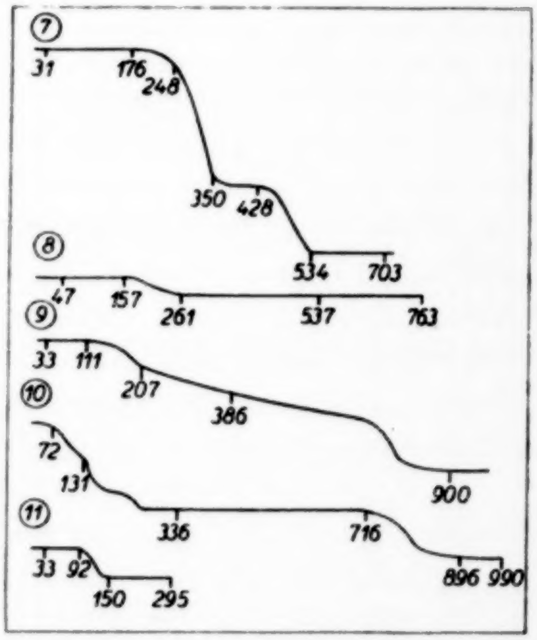
Phosphate diammonique

Le phosphate diammonique utilisé $(NH_4)_2PO_4H$ paraissait parfaitement sec et la courbe de thermolyse donne une droite horizontale jusqu'à 111°. Après quoi, commence la dissociation et la sublimation. Cette dissociation conduit vraisemblablement à un pyrophosphate complexe et il y a sûrement perte de phosphore par sublimation puisque vers 900°, quand le palier horizontal est atteint, on ne trouve que la moitié environ du poids d'anhydride phosphorique attendu (courbe 9). De toute façon, on ne peut pas sécher le sel au-dessus de 111°.

Ce phosphate présente les bandes d'absorption infrarouges suivantes: 850aF, 893-898 F et large, 925F, 1023f, 1053-1073F et large, 1189f cm^{-1}. Ce spectre avait déjà été interprété par DUVAL ET LECOMTE[5], toutefois, la bande faible à 1023 cm^{-1} n'avait pas été mesurée.

Alun de potassium

Le produit de départ, pris dans un flacon ouvert plusieurs fois, ne se montre pas déliquescent et s'accorde avec la formule $Al_2(SO_4)_3.K_2SO_4.24H_2O = 948.78$, mais il n'est pas stable pendant longtemps. A 48° la perte, d'eau se fait sentir; on n'observe pas de palier intermédiaire dans la



Courbes de thermolyse. (7) Anhydride arsénieux. (8) Sulfate de cadmium. (9) Phosphate diammonique. (10) Alun de potassium. (11) Tungstate de sodium.

déshydratation; toutefois, à 131°, un point de rebroussement dans la courbe s'observe quand la moitié de l'eau de cristallisation a disparu (courbe 10). Le départ des dernières traces d'eau est très lent et le palier des deux sulfates anhydres n'est vraiment horizontal qu'entre 336 et 716°; après quoi, il y a dissociation, perte de SO_3 et à 1000°, le résidu s'accorde à peu près avec $Al_2O_3.K_2SO_4$, avec une quantité variable de SO_3 d'une expérience à l'autre. Pour faire une liqueur titrée avec l'alun, il est recommandé de ne pas chauffer ce cel avant pesée au-dessus de 40° et de compter en hydrate à 24 H_2O ou de maintenir jusqu'à poids constant à 336° et de peser à l'état de sulfate double $Al_2(SO_4)_3.K_2SO_4 = 516.74$.

Il faut remarquer que dans le spectre infrarouge de l'alun nous trouvons bien les bandes caractéristiques de l'ion SO_4 pour 944 (m) et 1104 (TF) cm^{-1}. En outre, on observe des bandes supplémentaires beaucoup plus faibles que nous ne pouvons interpréter que par sa nature de sel complexe; citons notamment: une bande large à 910-919, trois bandes faibles à 941, 1188 et 1202 cm^{-1}.

Tungstate de sodium

Le tungstate de sodium correspond bien à la formule $Na_2WO_4.2H_2O$. On peut le peser directement; il est bien sec; si toutefois, on soupçonne une trace d'eau de mouillage, il ne faudrait pas dépasser 80° pour le séchage. La déshydratation est complète à 150°, température à laquelle commence le palier horizontal du produit anhydre (courbe 11).

Le spectre infrarouge a été enregistré successivement avec trois prismes, l'un au bromure de césium qui a fourni la bande de déformation de l'ion WO_4 à 540 cm^{-1}, puis avec un prisme de sel gemme qui a donné les cinq bandes suivantes: 810f, 826F, 858aF, 880aF, 932 m, enfin, avec le prisme de fluorure de lithium qui a donné les deux bandes 1670f et 3310F.

RÉSUMÉ

Dans cette deuxième étude de douze étalons, utilisés à des titres divers en chimie analytique, nous avons insisté sur le comportement thermique et fourni le spectre d'absorption infrarouge en vue de l'identification des corps et de leurs impuretés.

SUMMARY

In this second investigation of 12 standard solutions, used in various titrations in analytical chemistry, we have continued studies on the thermal behaviour and have obtained the infrared absorption spectrum with regard to identification of substances and their impurities.

ZUSAMMENFASSUNG

Bei dieser zweiten Untersuchung von zwölf Vergleichslösungen, welche in der analytischen Chemie bei verschiedenen Titern verwendet werden, haben wir auf das thermische Verhalten insistiert und haben das Spektrum der infraroten Absorption geliefert, im Hinblick auf die Identifikation der Stoffe und ihrer Verunreinigungen.

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THE MICRO-DETERMINATION OF CARBON AND HYDROGEN IN ORGANIC COMPOUNDS CONTAINING PHOSPHORUS

by

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We have noted that low carbon values are often obtained with certain types of organic compound containing phosphorus when burnt in the usual way in a combustion tube. In particular, sugar phosphates are subject to this effect, which is probably due to carbon particles becoming encased in the inorganic residue. The strong ignition of this residual carbon deposit in the boat, and, possibly on the walls of the combustion tube where some of the inorganic material may have volatilised, does not always effect its complete oxidation to carbon dioxide unless blasting is resorted to with the hottest possible flame. The carbon particles then give an incandescent glow and slowly disappear, but this treatment in the presence of phosphorus compounds has a deleterious effect on the tube. KLIMOVA[1] and his co-workers have reported a further complication when phosphorus is present. They obtained high hydrogen values when using a rapid combustion procedure, in the absence of any catalyst, and they suggest that this discrepancy may be attributed to the phosphorus pentoxide produced during the combustion of these compounds, passing into the first absorption tube.

When phosphorus is present SILBERT AND KIRNER[2] suggested the use of a platinum gauze cylinder filled with triplumbic tetroxide as an additional packing in a conventional PREGL combustion tube filling. However, if the combustion is carried out in a stream of oxygen in the presence of a platinum catalyst or using an empty tube method, the alternative procedure of mixing an oxidizing agent with the sample in the boat appears more promising. STEYERMARK[3] AND ROTH[4] have proposed, respectively, the use of potassium dichromate and vanadium pentoxide for this purpose. Their procedures are similar to those recommended for the combustion of organic compounds containing alkali or alkaline earth metals — namely, mixing the weighed sample with several times its weight of the reagent.

An examination has been carried out on these two reagents and several others in order to establish a simple, and reliable combustion procedure for this type of organic compound. The combustion method used is based upon a modification of the slow, catalytic microcombustion method of FRIEDRICH[5].

Di-potassium glucose 1-phosphate dihydrate was used as the principal test compound because some difficulty had been encountered with its combustion, and also, because of its ready availability in an analytically pure state.

REAGENTS EXAMINED

Although initially it was intended to examine the relative effectiveness of potassium dichromate and vanadium pentoxide when added to the weighed sample in the combustion boat, it was decided to extend the investigation to include several other reagents which have been noted either for their catalytic or oxidizing properties. The results obtained, following the admixture and combustion of each of these reagents with the test compound, di-potassium-glucose-1-phosphate dihydrate are listed in Table I.

TABLE I

REAGENTS EXAMINED WITH DI-POTASSIUM-GLUCOSE-I-PHOSPHATE DIHYDRATE

Results required: %C = 19.35 ; %H = 4.06.

Reagent added to weighed sample	*Weight mg*	*Results obtained*	
		%C	*%H*
Without reagent	6.019	18.64	4.00
	4.931	18.89	4.09
Cerium dioxide			
(i) Technical grade	5.748	19.04	4.16
(ii) Pure sample	6.460	19.12	4.04
Manganese dioxide	6.790	19.05	4.26
Tin dioxide	6.902	18.90	4.14
Silver chromate	4.675	19.15	4.20
Potassium dichromate	6.938	19.26	4.19
	6.842	19.38	4.09
	6.348	19.40	4.05
Vanadium pentoxide	5.501	19.15	4.12
	6.611	19.33	4.03
	5.450	19.40	4.12
Potassium persulphate	6.779	19.32	4.10
	5.877	19.37	4.20
Chromium trioxide	6.055	19.32	4.12
Copper oxide (precipitated)	6.220	19.30	4.00
	6.979	19.34	4.06
Tungstic oxide	6.584	19.23	3.96
	4.931	19.31	4.02
	6.539	19.27	4.00

Copper oxide, tungstic oxide, chromium trioxide, potassium dichromate, potassium persulphate, and vanadium pentoxide were the most promising reagents. Both chromium trioxide and potassium dichromate, in spite of the necessary precautions in their use, showed a tendency to creep and splutter, resulting in a serious attack upon the walls of the silica combustion tube. Although it did not react with the silica tube, vanadium pentoxide sublimed during the combustion period and the resultant discoloration of the tube made observation of the boat difficult, particularly when the final traces of carbon were being burnt off. The main objection to potassium persulphate, whose use with organic substances containing alkali or alkaline earth metals was first suggested by SIROTENKO[6], was the production of large quantities of sulphur trioxide during the combustion, resulting in an early exhaustion of the silver wool absorbent at the end of the combustion tube.

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The promising values obtained with a finely precipitated form of copper oxide were not confirmed with several other organic compounds containing phosphorus, which were more readily volatilized during combustion than was the test compound. Undoubtedly the copper oxide, when mixed with the di-potassium glucose 1-phosphate dihydrate, facilitated the complete oxidation of the carbon by reason of the formation in the boat of some blue copper phosphate. This suggested the effectiveness of copper oxide in this one instance was exceptional, and, that its use did not have general applicability.

Tungstic oxide did not have the disadvantages of the other effective reagents previously mentioned, namely, attack upon or discoloration of the combustion tube. When other types of phosphorus-containing compounds were examined, some of which were readily volatilized, the oxides of phosphorus, produced during the combustion, did attack the silica combustion tube. However, by placing an additional filling of tungstic oxide in a porcelain boat before the platinum contact, this attack was largely overcome, although it was advisable to replace this filling after every 6 to 8 analyses in order to maintain its effectiveness for this purpose. The general applicability of tungstic oxide as a reagent for difficultly combustible phosphorus-containing compounds is shown by the results outlined in Table II.

TABLE II

Compound	*Results obtained without reagent*		*Results obtained with tungstic oxide*		*Results required*	
	%C	*%H*	*%C*	*%H*	*%C*	*%H*
Di-potassium glucose 1-phosphate dihydrate	18.64 18.89	4.00 4.09	19.27 19.32	3.98 4.08	19.35	4.06
4-Nitrophenoxy-O:O-diethyl phosphorothionate (liquid)	40.37	4.73	41.14 41.17	4.79 4.81	41.23	4.84
N, N′, N″-Tri-*iso*propyl phosphoroamide	48.36	10.73	48.96 48.82	10.86 10.71	48.87	10.86
Tetra-acetyl galactose 6-diphenyl phosphoro diethyl mercaptal	51.42 51.48	5.52 5.59	52.52	5.70	52.46	5.68
N, N′-Di-*iso*propyl phenyl phosphorodiamidate	55.75	8.27	56.16	8.08	56.23	8.20
N-*Iso*propyl diphenyl phosphoroamidate	61.50 60.79	6.50 6.06	62.02 62.03	6.20 6.37	61.86	6.19

COMBUSTION APPARATUS

Preliminary investigations showed that manganese dioxide, the external absorbent for oxides of nitrogen recommended by BELCHER AND INGRAM[7] could satisfactorily replace the boats filled with lead dioxide as in the original FRIEDRICH combustion procedure. This assembly was preferred to the rapid combustion method of BELCHER AND INGRAM[8] which is used for all other types of compound (unless fluorine is present) because of the unavoidable attack on the more expensive vertical silica combustion. Although we ourselves only use it for these special cases, this slow combustion procedure can, of course, be used for all purposes and so we describe it in some detail. It is perhaps the simplest slow combustion assembly hitherto described. Some typical results for standard reference compounds are given in Table III.

TABLE III

Compound	*Weight mg*	*Results obtained* %*C*	%*H*	*Results required* %*C*	%*H*
Sucrose	4.406	42.21	6.40	42.10	6.48
	4.015	42.05	6.38		
Benzoic acid	3.428	68.76	4.96	68.84	4.95
	3.084	68.69	4.94		
m-Nitrobenzoic acid	4.838	50.38	3.03	50.30	2.99
	3.886	50.21	3.05		

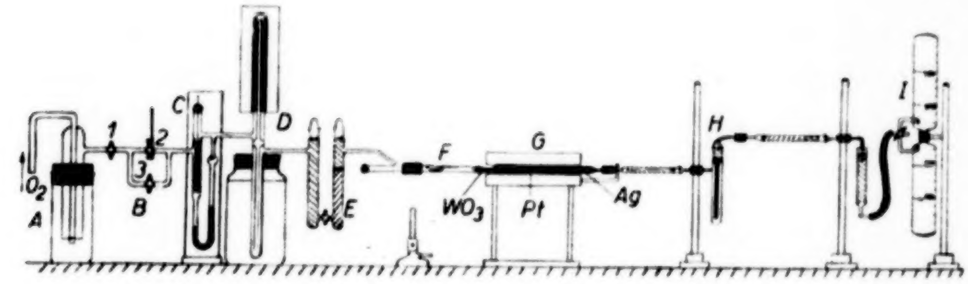

Fig. 1. Line diagram of apparatus.

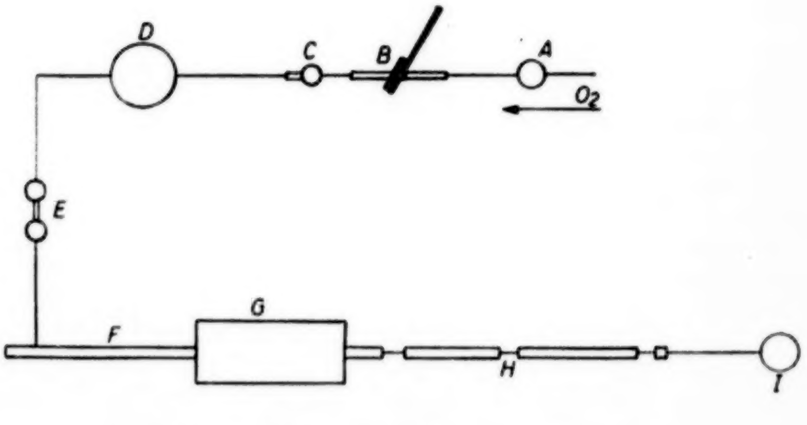

Fig. 2. Plan diagram of apparatus.

EXPERIMENTAL

Reagents

All the reagents were suitably dried before use, wherever possible by ignition, and stored over phosphorus pentoxide in desiccators. Tungstic oxide was prepared from reagent grade tungstic acid by ignition either in an open porcelain crucible, or, in a heated combustion tube in a stream of oxygen. Blank values were determined for each reagent by carrying out an actual combustion procedure, but in the absence of any organic substance. All the results given in Tables I and II have already been corrected for any such blank values.

Apparatus

The combustion apparatus, as outlined in the line and plan diagrams of Figs. 1 and 2, consists of the following items

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Pressure head (A), three-tap control (B), flowmeter (C) and pre-heater of the White-Wright type (D), scavenging U-tube (E), combustion tube (F), absorption and guard tubes (H) and finally a reversible aspirator bottle (I).

Belcher and Goulden[9] have earlier described the first five items relative to the purification and control of the oxygen supply. In order to produce a compact unit, the train, as shown in the plan-diagram, Fig. 2, is doubled back on itself.

Combustion tube

The transparent silica combustion tube used is of 580 mm length, 9 mm bore and with a side-arm of 3 mm bore. The beak of the tube is filled to its tip with silver wool in order to prevent water condensation and is followed by an additional 55 mm length of silver wool for the removal of sulphur oxides and halogens. To complete the main filling of the tube there is a platinum foil contact, 140-145 mm long, made by loosely rolling a 120 × 50 × 0.08 mm sheet of the metal across its diagonal and with platinum wire hooks attached to its ends to facilitate the easy removal of the contact from the tube for cleaning in boiling nitric acid (1:1) after every 10-12 analyses. Finally a porcelain boat, 30-40 mm long, filled with tungstic oxide, is placed in front of the platinum contact and over the end region of the long furnace in order to absorb any phosphorus oxides produced during the combustion of phosphorus-containing compounds. This filling should be renewed every 6-8 determinations.

The combustion tube is placed in a long furnace, electrically heated to 750° ± 20° C, so that 50-55 mm of the beak end projects from its end. A copper rod, connecting to a small sliding block for heating the capillary end of the water absorption tube, fits into a special pocket in the beak end of the long furnace.

Absorption and guard tubes

The normal Pregl-type absorption tubes are used, the filling being kept in place by small wads of glass wool. When nitrogen-containing compounds are to be analysed, manganese dioxide, in a suitably designed tube previously described by **Belcher and Ingram**[7], is placed between the anhydrone and soda asbestos tubes.

Reversible aspirator bottle

This aspirator bottle, as shown in Figs. 1 and 3, is developed from those suggested by **Fischer**[10] and **Belcher and Goulden**[9]. It consists of two suitably calibrated measuring bottles connected by a thick-walled glass tube, protected with thick rubber tubing so that it can serve as a central clamping rod for the rotation of the bottles. The attachment of a 4-way tap between the two bottles eliminates the necessity of removing the rubber tubing connection to the guard tube between determinations, as in the earlier design.

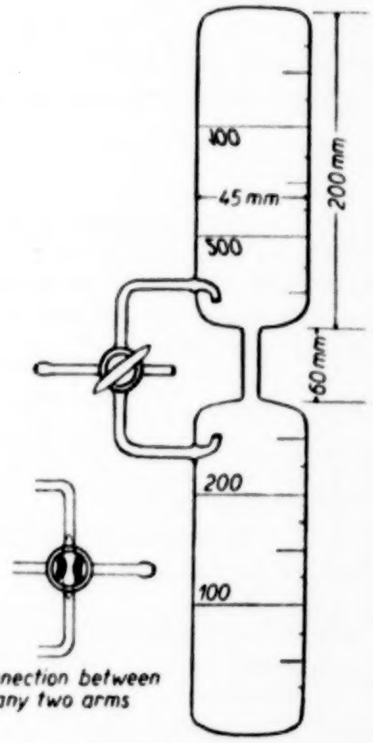

Fig. 3. Reversible aspirator bottle.

Procedure

When the furnace has reached the required temperature, the whole apparatus is connected up, the three taps for the oxygen supply are closed and oxygen is admitted from a cylinder at the rate of 2-5 bubbles per second. The aspirator bottle is inverted so that the water (coloured blue for convenience) is in the upper chamber and the 4-way tap turned so that oxygen can enter this chamber.

With tap 1 fully open, the oxygen supply is adjusted carefully to a flowrate of 4 to 5 ml per minute, using the long-handled controlling clamp attached to tap 2. After sweeping out with oxygen for 10 to 15 minutes, the absorption tubes are removed, wiped and weighed according to the customary procedure of **Pregl**.

Weigh 3-6 mg of the dried sample into a platinum boat and cover completely with 5 to 8 times its weight of the dried, ignited tungstic oxide. Re-connect the absorption tubes, open tap 3 and remove the rubber bung from the combustion tube. Insert the boat and its contents quickly to within 80 mm of the long furnace and replace the bung. With tap 3 closed, test for any leaks prior to the commencement of the combustion. Open tap 1 and adjust the flow rate to 4 ml per minute by means of tap 2. Start the initial burning of the sample with the small flame of a mantled Bunsen burner and using a 50 mm length of brass tube around the combustion tube to ensure even heating of the tube. The preliminary burning of the sample takes about 15 minutes, and the second heating with the Bunsen burner at full pressure, another 5 to 10 minutes. The burner should be kept under the boat for at least 2 minutes to ensure that all carbon particles are completely burnt. 90 to 100 ml of oxygen are collected in the aspirator bottle during this period. Sweep out the combustion tube until the total volume of oxygen passed in the determination is 200 ml. Remove the absorption tubes and repeat the timed wiping and weighing procedure.

An accuracy of ± 0.2% for the carbon and hydrogen values is readily attainable with this modified FRIEDRICH combustion procedure and it is recommended in place of the more conventional and time-consuming PREGL micro-combustion method when the rapid, "empty tube" procedure is inadvisable, as in the case of phosphorus-containing organic compounds. The apparatus possesses the added advantage that it can be set up for use very quickly without the necessity of a long burning-out period, as with the PREGL tube filling.

SUMMARY

Several reagents have been examined for use in the micro-determination of carbon and hydrogen in organic compounds containing phosphorus for which low carbon values had previously been reported. Tungstic oxide was found to be the most convenient reagent for this purpose. A modification of the procedure of FRIEDRICH was used throughout this investigation which is suitable for universal application.

RÉSUMÉ

Plusieurs réactifs ont été examinés en vue de leur utilisation lors des microdosages de carbone et d'hydrogène dans des substances organiques renfermant du phosphore. C'est l'anhydride tungstique qui a donné les meilleurs résultats. Une modification du procédé de FRIEDRICH (convenant pour une application universelle) a été utilisée pour ces recherches.

ZUSAMMENFASSUNG

Es wurden verschiedene Reagenzien untersucht im Hinblick auf ihre Verwendung für Mikrobestimmungen von Kohlenstoff und Wasserstoff in organischen Verbindungen, welche Phosphor enthalten. Das Wolframsäureanhydrid gab die besten Resultate. Es wurde eine Modifizierung des Prozesses FRIEDRICH (welcher für eine universelle Anwendung geeignet ist) für diese Forschungen verwendet.

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PAPER CHROMATOGRAPHY OF INORGANIC IONS

XII. — THE SEPARATION OF Be, Ge, In AND Ga

by

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In previous papers of this series we published the R_F values of numerous ions with butanol-N HCl as solvent[1]. This solvent was also found useful for the separation Ge-As in the preparation of carrier-free ^{74}As[2]. HECHT *et al.* had also measured the R_F value of Ge with butanol-10% HBr and butanol-10% HNO_3 as solvents[3]. A remarkable coincidence of R_F values in butanol-HCl, -HBr, and -HNO_3 was observed (0.26 in all cases). If this observation is correlated with other data on the extraction and R_F values of ions one must conclude that Ge(IV) is in the same ionic state in all three solvents and that this state presumably does not contain an anionic group. Thus a germanic acid type of ion, possibly a hydroxy-cation, appears to exist in dilute HCl, HBr and HNO_3. Since the volatility of $GeCl_4$ in conc. HCl is used for a separation by distillation it was considered likely that the R_F value would vary with the HCl concentration in the solvent, as a gradual transition from the hydroxy-cation to the covalent chloride must occur. In butanol-N HCl there are two ions with the same R_F value as Ge; these are In(III) and Be(II). Ga(III) has been shown to have an R_F value which varies with the HCl concentration[4]. It was also included in this study since its separation from In, Ge and Be is often of interest.

The work here described is the measurement of the R_F values in mixtures of butanol-HCl containing various concentrations of HCl. By choosing a suitable concentration of HCl (3N) it is possible to separate the four elements studied.

EXPERIMENTAL

The following four solvents were prepared:

(I) Butanol 100 ml, HCl conc. 10 ml and water 90 ml (two phases).
(II) Butanol 100 ml, HCl conc. 30 ml and water 70 ml (two phases).
(III) Butanol 100 ml, HCl conc. 50 ml and water 50 ml (one phase).
(IV) Butanol 100 ml, HCl conc. 100 ml (one phase).

Solvents (III) and (IV) in addition to containing more HCl than (I) and (II) also are more polar owing to the existence of one single phase holding all the water added. Thus in these two solvents one may expect a separation due to polarity differences as well as to complex formation.

Table I shows the R_F values obtained:

TABLE I

Ion	*(I)* *butanol* *N HCl*	*(II)* *butanol* *3N HCl*	*(III)* *butanol* *6N HCl*	*(IV)* *butanol* *12N HCl*
Be^{+2}	0.15	0.30	0.58	0.44
In^{+3}	0.24	0.40	0.55	0.42
Ge^{+4}	0.26	0.54	0.93	1.0
Ga^{+3}	0.27	0.70	1.0	1.0

As will be evident, the best separation of all four ions is achieved with butanol-3*N* HCl.

DISCUSSION

The variation of the R_F value with increasing HCl concentration makes an interesting comparison with the anion exchange equilibria measured by KRAUS *et al*[5]. Ga (III) is not appreciably adsorbed (*i.e.* it is cationic) below 3*N* HCl and reaches a maximum (*i.e.* it is completely anionic) at 6*N* HCl where we can also note an R_F of 1.0. Indium was found by KRAUS *et al.*[5] to be relatively little adsorbed at all HCl concentrations between 0 and 12*N*; our R_F value curve is analogous. Be does not adsorb at all on Dowex-1 in 7*N* and 12*N* HCl; thus an anionic form does not seem to exist and our R_F values seem to be influenced mainly by the solubility of the cation in the organic solvent. Be(II) having a small ionic radius should exhibit this solubility in butanol.

Germanium (IV) had not been studied on anion exchange resins. As pointed out in the introduction of this paper, chromatographic evidence points to the existence of a cationic form, which has the same R_F value in numerous acid media. It should be possible to predict with our R_F values the anion exchange properties of Ge (IV) in relatively concentrated HCl and we suggest that Ge will yield an equilibrium curve similar to Ga(III) but with a maximum at a slightly higher HCl concentration.

SUMMARY

A paper chromatographic separation of Be, Ge, In and Ga is described and the behaviour of the elements in various butanol-HCl mixtures discussed.

RÉSUMÉ

On décrit une séparation chromatographique sur papier du Be, Ge, In et Ga. Le comportement de ces éléments dans divers mélanges butanol-HCl est examiné.

ZUSAMMENFASSUNG

Es wird eine Trennung von Be, Ge, In und Ga mittels Papierchromatographie beschrieben. Das Verhalten dieser Elemente wurde in verschieden Mischungen Butanol-HCl untersucht.

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DETERMINATION OF THE ALKALINE EARTHS IN GLASS

by

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In a previous paper[1], an ion-exchange method was described for the quantitative separation of the alkaline earths from each other. This paper presents the application of the ion-exchange separation to the determination of the alkaline earths in glass.

Preliminary experiments indicated that most of the elements of glass appear with the calcium in the first fraction of the eluate. For this reason, it was deemed advisable to isolate the alkaline-earth group before the application of the chromatographic separation. Furthermore, overloading of the column was avoided by the group separation.

EXPERIMENTAL

Apparatus and reagents

An exchange column, 2.54 sq.cm in cross-section area, was filled to a depth of 19 cm with colloidal aggregates of Dowex-50, lot 50572, previously passed through a 120-mesh sieve.[1] Reagent-grade chemicals were used.

Analysis of N.B.S. sample 128

Sample 128, a soda-lime glass, from the National Bureau of Standards was analyzed by the following procedure. A 1-g sample was decomposed by hydrofluoric and sulfuric acids. After evaporation to fumes of sulfur trioxide, the volume of sulfuric acid was adjusted to 5 ml, and 40 ml of 80% ethyl alcohol were added. The precipitate, which contains all the alkaline earths and an appreciable amount of other cations, was filtered and washed thoroughly with 80% alcohol containing 10% sulfuric acid.

The bulk of the precipitate was washed from the filter paper into a beaker. The paper was ignited, and its ash was added to the precipitate. Then 7 g of ammonium iodide and 40 ml of concentrated hydrochloric acid were added to make the total volume about 150 ml. The mixture was boiled nearly to dryness; then it was cautiously heated to complete dryness. The ammonium salts were volatilized on a hot plate. This treatment reduces the insoluble sulfates[2] and converts them to soluble iodides.

The residue was dissolved in dilute hydrochloric acid and treated with bromine. The insoluble hydroxides were precipitated twice with ammonia. The combined filtrates were evaporated to 40 ml, and pellets of sodium hydroxide were added to make the solution strongly basic. Then 3 g of sodium carbonate were added. The precipitate of alkaline-earth carbonates was filtered, washed, and dissolved in hydrochloric acid. This solution was evaporated to dryness, dissolved in 5 ml of water, and treated as previously described.[1]

Since no standard samples of glass containing all three alkaline earths were available, a synthetic sample was prepared by adding a small amount of strontium to sample 128. This was analyzed by the same procedure.

Analysis of N.B.S. sample 89

The presence of lead in this sample required a few alterations from the foregoing procedure. Perchloric acid was substituted for sulfuric acid in the expulsion of fluoride. The residue was dissolved in dilute nitric acid, and a double precipitation with hydrogen sulfide was performed to remove the lead. In one case, electrolysis at 15 amperes for 30 minutes from a perchloric acid solution with a mercury cathode (Eschbach Dynacath) was applied to remove the lead. In all other respects sample 89 was treated like 128.

Results

The results of these analyses are given in Table I.

TABLE I

ANALYSES OF STANDARD SAMPLES

Sample Number	*CaO, %*		*BaO, %*		*SrO, %*	
	Certified	*Found*	*Certified*	*Found*	*Added*	*Found*
128	4·76	4·79	0.49	0.49		
		4·71		0.49		
		4·77		0.49		
128		4·72		0.48	0.94	0.92
		4·75		0.47		0.91
89	0.21	0.23	1.40	1.40		
		0.22		1.38		
		0.20		1.38		
		0.23*		1·37*		

* Lead was removed by the mercury cathode.

DISCUSSION

Several other procedures for isolating the alkaline-earth group were tried and discarded because of low results. For example, after the removal of silicon from sample 128 by treatment with perchloric and hydrofluoric acids, boron was removed by volatilization of methyl borate. The insoluble sulfates, derived from the SO_3 present in the sample, were dissolved by fusion with sodium carbonate and added to the main solution. Iron and aluminium were precipitated twice with ammonia. Then the alkaline earths were precipitated by the addition of sodium hydroxide, sodium carbonate and alcohol.

In the procedure finally adopted, ammonium iodide and hydrochloric acid were used rather than hydriodic acid[2], to reduce the insoluble sulfates. Reagent-grade hydriodic acid contains hypophosphorous acid as a preservative; this causes the precipitation of the alkaline earths when ammonia is added to precipitate the iron and aluminium.

Additional details of the work reported in this paper may be found elsewhere[3].

SUMMARY

The alkaline-earth group was isolated, after removal of silica, by precipitation as sulfates from an alcoholic solution. These sulfates were reduced and dissolved by treatment with hydriodic acid. The alkaline earths were separated from each other by ion-exchange chromatography. The results are in good agreement with the values reported by the National Bureau of Standards.

References p. 441

RÉSUMÉ

Les éléments alcalino-terreux peuvent être séparés, après élimination de la silice, par précipitation des sulfates en solution alcoolique. Ils sont ensuite séparés les uns des autres par échange d'ions chromatographique. Les résultats correspondent bien aux valeurs données par le ,,National Bureau of Standards''.

ZUSAMMENFASSUNG

Nach der Verflüchtigung der Kieselsäure, isoliert man die Gruppe der alkalischen Erden durch die Ausfällung ihrer Sulfate aus alkoholischer Lösung. Man reduziert und löst diese Sulfate mit Jodwasserstoffsäure. Die Trennung der alkalischen Erden von einander gelingt durch Austauschchromatographie. Die Analyse der Eichproben zeigt dass die Methode genau ist.

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THE SEMI-MICRO DETERMINATION OF FLUORINE, CHLORINE, AND NITROGEN IN ORGANIC COMPOUNDS

II. THE USE OF CATION EXCHANGE RESINS*

by

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The determination of halogens in fluorine-containing organic compounds has always been tedious and difficult. In the case of fluorine, one is faced, after carrying out the sodium fusion in a nickel bomb such as that described by BELCHER AND TATLOW[2], either with the awkward end-point of a thorium nitrate titration, or with the longer procedure of the lead chloro-fluoride process. As has been shown by BELCHER *et al.*[3,4] both methods will give excellent results in the hands of experienced analysts especially since the possible error involved in seeing the colour change of the sodium alizarin sulphonate has been so much reduced by their colour comparison procedure. For the chlorine, direct argentometric titration of the chloride in a fusion solution using dichloro-R-fluorescein is, in our experience, impossible; other direct methods do not give sufficiently sharp end-points, and again recourse has to be made to longer, indirect methods such as those described by BELCHER, MACDONALD AND NUTTEN[5], or BROWN AND MUSGRAVE[1]. We now find however that the determination of these elements in organic compounds can be simplified considerably by making use of cation exchange resins which permit the determination of total halogen by alkalimetry. The resins also remove ions which are due to the use of excess of sodium in the bomb and its consequent neutralization, and which interfere in the chloride estimation. SAMUELSON[6] has used cation exchange resins for the estimation of chloride, bromide, and iodide, and OSBORN[7] has mentioned their use for the estimation of fluoride, but both authors have simply taken solutions of the pure inorganic salts concerned and have not considered any of the difficulties which inevitably occur when the methods are applied to routine analysis of organic compounds in the laboratory. There are quite a number of these complications, and one point which must continually be borne in mind when using these resins is that any salt whatsoever will interfere since, on passing through the column, it will give rise to an acid.

We have always used polythene columns of the dimensions shown in Fig. 1 for our exchange columns, containing about 20 g of Amberlite I.R. 120 (H) as packing. However, when analyses are carried out on the semi-micro scale it is doubtful if polythene is necessary since we have found that the dilute hydrofluoric acid can be collected and titrated in glass flasks without introducing any error. Such an amount of resin, in the acid form, is equivalent to about 30 ml of N Na^+ (or 150 ml of a fusion solution which is generally about 0.2N in Na^+) but our columns are regenerated after 70 ml of fusion solution has passed through them. This regeneration involves the addition to the column of 250 ml N HCl which is then eluted with 1 l of distilled water.

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* For I, see *Anal. Chim. Acta*, 12 (1955) 29.

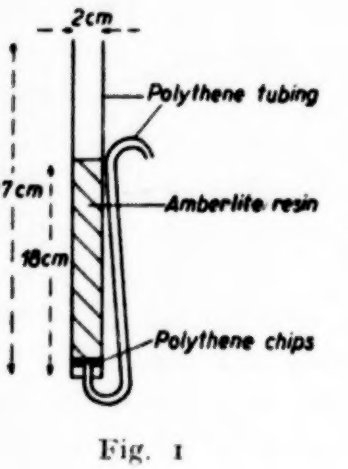

Fig. 1

When 10 ml aliquots of either 0.01N sodium chloride or 0.01N sodium fluoride were washed through the resin with 70 ml of water from a dropping funnel and the resultant eluates titrated with 0.02N caustic soda using methyl red screened with either bromocresol green or methylene blue as indicator, the concentrations obtained for chloride and fluoride ions respectively were identical with those expected by theory and also with those obtained by titration of the original solutions with silver nitrate, using dichloro-R-fluorescein as indicator, or with thorium nitrate by the method of BELCHER *et al*[3]. In order to obtain reproducible results with these dilute solutions, it was necessary to boil all the water used in preparing solutions to remove carbon dioxide, to use carbonate-free caustic soda and to carry out blank runs on the distilled water to ensure its purity. Nevertheless, even when these precautions were applied to the solutions obtained by fusing organic compounds containing either chlorine or fluorine with sodium, poor results, which were eventually traced to two causes, were obtained. The first was due to water soluble salts in the filter papers used to separate the carbon residues. Various grades of filter paper were washed with 80 ml distilled water, the washings were made up to 100 ml and then 10 ml aliquots were washed through the ion exchange column. The acid present was equivalent to between 0.02 and 0.08 ml of 0.02N NaOH depending on the grade of filter paper. This source of error was easily removed by using sintered glass funnels of No. 1 or No. 2 porosity.

The second source of error lay in the method used to destroy the excess sodium used in the fusion. Although pure alcohol when added to a synthetic fusion mixture did not affect the eventual acid-alkali titration, when alcohol was used to destroy the excess of sodium in an actual fusion mixture, high results were obtained. In a test run in which glucose was fused in the normal way, the excess of sodium was destroyed with alcohol and the fusion solution was made up to 100 ml; a 10 ml aliquot was equivalent to approximately 0.2 ml of caustic soda solution. An alternative method for destroying the sodium is described by BELCHER *et al*[5]. and involves packing the bomb with solid carbon dioxide and then adding water carefully. This method results in the formation of a considerable amount of sodium carbonate, which has to be removed as carbon dioxide by boiling the acidified solution. Although this method is quite safe with the very dilute fluoride solutions obtained on the micro scale, experience has shown that on a larger (semi-micro) scale there may be a loss of up to two per cent of fluoride ion on boiling[8]. The main fault with this method however, as far as we are concerned, is that the solid carbon dioxide contains non-volatile, soluble, impurities which on passing through the resins are converted to acids, and cause results to be too high. Thus after destroying some sodium in a nickel basin by this method, making up the solution to 100 ml, passing a 10 ml aliquot through the resin, and then boiling, the volume of $0.02N$ NaOH required could not be reduced below 0.06 ml. We have therefore devised an apparatus, Fig. 2, for destroying the excess of sodium in an atmosphere of nitrogen at room temperature. Water is added from the dropper C at the rate of about one drop in twenty seconds at first, but more quickly as the sodium is destroyed. If the operation is carried out carefully no splashing occurs; this needs to be avoided since it results in attack on the glass by the concentrated alkali with consequent slight buffering of the end-point. When this buffering does occur the methyl red-methylene blue indicator cannot be used. By this method, the amount of carbon dioxide absorbed is very small and is easily removed by bringing the solution to the boiling point, after putting it through the resin, and cooling immediately; the introduction of impurities is also avoided. When these precautions were taken, excellent results, which are shown in the table, were obtained.

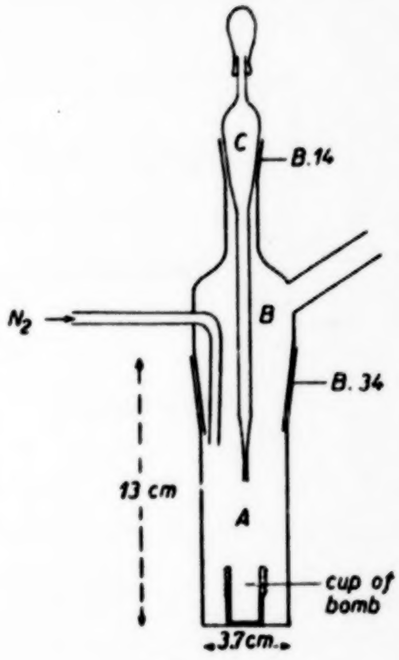

Fig. 2

When both chlorine and fluorine were present in the organic compound, the titration of the eluate gave the equivalent of the total halogen present and an accurate method for the determination of chloride was necessary in order to be able to find the fluoride by difference. As has already been stated by Brown and Musgrave, it is impossible to take an aliquot of the solution from the sodium fusion, neutralize it with nitric acid and titrate with silver nitrate using dichloro-R-fluorescein as indicator, because the end-points are quite haphazard, presumably because of varying high concentrations of nitrate ions from the neutralization, However, it was found that if an aliquot of the solution from the fusion was first put through the ion exchange column and then neutralized with the amount of alkali already known from the determination of total halogen, the dichloro-R-fluorescein indicator worked perfectly well, provided the solution was first evaporated until it contained approximately 2 mg of chloride ion per 10 ml. This figure was chosen because the solution is then sufficiently concentrated to give a good colour change without the silver chloride being thrown out of solution before, or at, the end-point as it is when more concentrated solutions are used. The success of the method is simply due to the removal of the excess alkali by the resin, with the result that the silver nitrate titration is carried out on a more or less pure solution of sodium halides, the only condition under which adsorption indicators function accurately.

An alternative procedure, and one which is better when solutions containing only small amounts of chloride ion (up to 1 mg 10 ml) are being titrated, is to neutralize the eluate from the ion exchange column with caustic soda using methyl red screened with methylene blue and then proceed directly to the determination of the chloride using mercuric oxycyanide as described by Belcher, Macdonald and Nutten[5]. Ma and Zuazaga's indicator can be used in this process, but does not give such a sharp end-point and results tend to be slightly low. It should perhaps be stated at this stage that successful attempts have been made by DeGeiso, Rieman and Lindenbaum[9] to separate chloride, bromide and iodide ions on an anion exchange

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column. Similar methods would no doubt permit the separation of chloride and fluoride ions but the procedure takes three hours which is too long for a routine analysis.

The cation exchange method can also be applied to organic compounds which contain nitrogen as well as fluorine and chlorine. As already stated[1], the nitrogen cannot be determined as cyanide if oxygen is present in the compound, since a certain amount of cyanate is then formed. If no oxygen is present, the cyanide is determined by DENIGES' method, but both cyanide and cyanate must be removed before the halogens can be determined. The cyanide can be removed by treating an aliquot of the alkaline solution from the fusion with formaldehyde and allowing it to stand for about 30 min when the cyanide is converted to hexamethylene tetramine. The mixture can then be put through the ion exchange column where any sodium cyanate is converted to cyanic acid which immediately decomposes to ammonia and carbon dioxide. The ammonia is retained in the column and the carbon dioxide passes through in solution. This is removed with the rest of the absorbed carbon dioxide when the solution is heated to boiling point and then cooled before titrating. Such treatment does not affect the fluoride determination. Precautions in the removal of cyanide and carbon dioxide need only be taken when fluoride is present; if this is not so the solution containing chloride, cyanide, and cyanate need simply be boiled, after passing through the column, until the hydrocyanic acid is removed.

Reagents

Sodium hydroxide solution. 0.02*N*.
Silver nitrate solution. 0.01*N*.
Mercuric oxycyanide solution. 20 g of mercuric oxycyanide were shaken with 1 litre of distilled water and the solution neutralized approximately with 0.01*N* sulphuric acid using methyl red-methylene blue indicator, and filtered into a brown glass bottle.
Sodium chloride solution. 0.01*N*.
Sulphuric acid solution. 0.02*N*.
Ammonia solution. 6*N*.
Formaldehyde solution. 0.1*M*.

Indicators

Methyl red-methylene blue. 0.125 g of methyl red was dissolved in 50 ml of 90% ethyl alcohol; 0.083 g of methylene blue was dissolved in 50 ml of 90% alcohol. Equal parts were mixed immediately before use.

Methyl red-bromocresol green. 0.04 g of methyl red and 0.06 g of bromocresol blue were dissolved in 100 ml of 95% alcohol.
Dichloro-R-fluorescein. 0.1 g in 100 ml of 70% alcohol.

EXPERIMENTAL METHODS

Take a known weight of the organic compound containing about 10 mg of the elements to be determined, using a nickel weighing capsule if the compound is a liquid. Fuse with excess of sodium for 1-1½ hours at 600-700° C in a nickel bomb. When cold, wash the outside of the bomb with distilled water and discard the washings. Remove the lid and wash the underside with a little water, allowing the washings to run into tube A, Fig. II. Now place the cup of the bomb in A, put on the lid B and pass a stream of nitrogen to displace the air. Add water, drop by drop, from the dropper C, which is fitted with a rubber teat, taking care that no sodium splashes out

TABLE I

In those titrations marked with an asterisk the indicator was methyl red-methylene blue. In all other acid-alkali titrations methyl red-bromocresol green (Ma + Zuazaga's indicator) was used.

Compound (g)	*% Cl*				*% F*		*% N*		*Removal of Cyanide*
	Calc.	*Found*			*Calc.*	*Found*	*Calc.*	*Found*	
		NaOH	*$AgNO_3$*	*$HgO.Hg(CN)_2$*					
Benzene Hexachloride									
(0.08863)	73.2	73.2	73.2						
(0.05232)	73.2	73.3	73.5						
Chlorobenzene									
(0.03771)	31.55	31.5	31.4	31.5					
		31.5*		31.5					
(0.05880)	31.55	31.5	31.4						
(0.05440)	31.55	31.5							
m-Chlorobenzoic acid									
(0.06709)	22.65	22.6	22.6						
(0.08194)	22.65	22.5	22.5						
(0.08492)	22.65	22.7	22.6	22.6*					
		22.7*		22.4					
(0.09473)	22.65	22.4	22.4	22.3*					
		22.5*		22.2					
1,1-Difluorocylcohexane									
(0.05909)					31.67	31.5			
(0.05859)					31.67	31.5			
p-Chlorofluorobenzene									
(0.06490)	27.2		27.0		14.57	14.6			
(0.05640)	27.2		27.3		14.57	14.4			
p-Chloronitrobenzene									
(0.12407)	22.54	22.5	22.5						HCN boiled off
(0.09851)	22.54	22.4	22.3						HCN boiled off
		22.5							HCHO added
(0.10514)	22.54	22.5	22.4	21.9					HCN boiled off
		22.4*		22.5*					HCN boiled off
		22.6							HCHO added
		22.6*							HCHO added
Anilinium trifluoroacetate									
(0.05310)					27.54	27.5			
						27.5*			
(0.07057)					27.54	27.8			
Anilinium chloride									
(0.11464)	27.40	27.4	27.4				10.81	10.7	HCN boiled off
		27.5							HCHO added
(0.05221)	27.40	27.4	27.3	27.4			10.81	10.7	HCN boiled off
		27.4*		27.5*					HCN boiled off
		27.5							HCHO added
		27.4*							HCHO added
2-Chloro-5-trifluoromethylacetoacetanilide									
(0.06069)	12.7		12.5		20.4	20.4			HCHO added
(0.04759)	12.7		12.3		20.4	20.1			HCHO added
Anilinium chloride + 1,1-difluorocylcohexane									
(0.02170) + (0.02972)	27.40			27.2	31.67	31.6	10.81	10.9	HCN boiled off
				27.3*		31.5*			for Cl^-detn.
									HCHO added for
(0.02143) + (0.02969)	27.40		27.2	27.3*	31.67	31.5*	10.81	10.7	NaOH titn.

onto the glass walls. When all of the sodium is destroyed, cover the nickel cup with water and heat A in a water bath to 50° C for about two minutes so as to complete the extraction and coagulate the solid matter. Cool, filter, and wash quantitatively, using a funnel with a sintered glass filter plate of No. 1 or No. 2 porosity, into a 100 ml standard flask.

If chlorine or fluorine is present alone

Take an aliquot (10 ml) of the fusion solution and run it from the pipette onto the Amberlite resin. Elute it with 70 ml of boiled distilled water over a period of 10 minutes, collect all of the eluate, heat it to boiling point and cool immediately. Titrate the whole of this with standard 0.02*N* NaOH solution using methyl red screened with either bromocresol green or methylene blue as indicator (10 drops).

If chlorine and fluorine are present

Proceed as above to determine the total halogen content, and then take a second aliquot, pass it through the column, neutralize with the previously determined volume of 0.02*N* NaOH, and then evaporate until the solution contains approximately 2 mg of chloride per 10 ml. Titrate this solution with 0.01*N* silver nitrate solution using ten drops of dichloro-R-fluorescein as indicator, the end-point being the disappearance of the green fluorescence with the appearance of a buff colour on the colloidal silver chloride.

Alternatively, after neutralization using methyl red screened with either methylene blue or bromocresol green as indicator, the chloride can be determined in the same aliquot using mercuric oxycyanide as described by BELCHER *et al*[5]. Methyl red-methylene blue is the better indicator.

If chlorine, fluorine, and nitrogen are present

If there is no oxygen in the compound and the cyanide is to be determined, this is done by DENIGES' method, an aliquot (25 ml) of the fusion solution being treated with 6*N* ammonia solution (7 ml) and 0.1*N* KI solution (2 drops), and titrated with silver nitrate solution to a permanent turbidity.

For the determination of chloride and fluoride, an aliquot (10 ml) of the fusion solution is treated with 0.1*M* aqueous formaldehyde (3 ml), allowed to stand at room temperature for 30 minutes to ensure complete reaction of the cyanide, and then washed through the ion exchange column and treated as before.

It is necessary to carry out a blank determination on the formaldehyde solution, since it contains an appreciable quantity of formic acid.

Two of us (R.E.B. & F.C.) wish to thank the Department of Scientific and Industrial Research for maintenance grants.

SUMMARY

The organic compounds are fused in a nickel bomb with sodium in the usual way. If no oxygen is present, the nitrogen is determined as cyanide by DENIGES' method. After destruction of cyanide with formaldehyde the total chloride and fluoride is determined by passing the solution through a cation exchange column and determining total acidity in the eluate. The chloride in the same or a separate eluate is then determined by treatment with mercuric oxycyanide or by titration with silver nitrate.

RÉSUMÉ

Les composés organiques sont fondus avec du sodium dans une bombe de nickel, par le procédé habituel. Pour le dosage de l'azote dans les substances ne renfermant pas d'oxygène, on utilise la méthode de DENIGES. Après destruction de l'ion cyanhydrique par le formaldéhyde, la teneur totale en ions chlorhydrique et fluorhydrique est déterminée par dosage de l'acidité de la solution, après élution à travers une colonne d'échangeur de cations. L'anion chlorhydrique est ensuite dosé, sur la même ou sur une autre prise, par addition d'oxycyanure de mercure ou par titration avec le nitrate d'argent.

ZUSAMMENFASSUNG

Die organischen Verbindungen werden, wie gewöhnlich, mit Natrium in einer Nickelbombe geschmolzen. Für die Bestimmung des Stickstoffes in den Substanzen, die keinen Sauerstoff enthalten, wendet man die Methode nach DENIGES an. Nach der Zerstörung des Cyanid-Ions

mit Formaldehyd, wird der gesamte Gehalt an Chlor-und Fluor-Ionen mittels einer Dosierung des Säuregehaltes der Lösung bestimmt, nach dem Durchfluss durch eine Kationenaustauschsäule. Darauf wird das Chlor-Ion in der gleichen, oder in einer anderen Substanzentnahme bestimmt, durch eine Zugabe von Quecksilberoxycyanid, oder durch eine Titration mit Silbernitrat.

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COPPER SALICYLALDOXIME AND ITS USE IN THE HETEROMETRIC MICRODETERMINATION OF COPPER IN THE PRESENCE OF FOREIGN METALS

by

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INTRODUCTION

The chemical behaviour of some metals towards salicylaldoxime has already been studied. The gravimetric separation and determination of copper, zinc or lead has been the subject of many investigations[1]. Our aim was to study the *heterometric* determination of metals with salicylaldoxime. It appears to us that the heterometric behaviour of salicylaldoximates at different pH's may contribute to our knowledge of the chemical structure and composition of many compounds of which little is yet known. This is the first report on salicylaldoxime and it deals with the determination of copper.

Although the heterometric determination of copper with oxine is more sensitive and more accurate, nevertheless, as the following material shows, *one* mg of copper in 10 ml solution may be determined with an error of 0-3%. The analysed solution may contain $\sim$ 99% bivalent or $\sim$ 90% trivalent foreign metals. The titration takes 10-20 minutes.

EXPERIMENTAL

The same apparatus and method were used as in previous reports[2]. In addition the heterometer was provided with a thermostat which maintained the temperature of the titrated solution at 20 °C (± 0.1°). (However, we found that the same accuracy was obtained without the use of the thermostat.) In all titrations with copper a blue filter was used. Generally no other filters were used even in the presence of coloured solutions. It was assumed that the coloured foreign salts do not participate in the reaction. Only in the presence of iron (exps. 24-27) a deep red filter was used and in the presence of chromium (exps. 20-23) a green filter was used.

The solution was stirred vigorously during the titration and the readings on the galvanometer were taken only when they became constant. The chemicals used were either analytical reagents or chemically pure. The salicylaldoxime was a Kodak reagent which was dissolved in a few ml alcohol and then diluted with distilled water.

RESULTS

Heterometric pH-study

pH-titrations were made in order to study the pH-conditions necessary for carrying out heterometric titrations. Two different buffer mixtures were used (exps. 1 and 4) and the results obtained can be taken from the curves. A blue filter (Fisher) was used in all the heterometric titrations. Analogous results were obtained using a green filter (Fisher). Whichever filter was used, some light was absorbed after the dissolution was completed.

Since the pH's necessary for the dissolution of the precipitates may be different from the pH's needed for precipitation, both cases were studied (Fig. 1 curves 1 and 2) separately. The pH's for the blank heterometric titrations are shown in curves 3 and 5. Analysing curve 1, it is seen that the precipitate once obtained at low pH's is completely insoluble below pH ∿ 10.2. At higher pH's the precipitation redissolves.

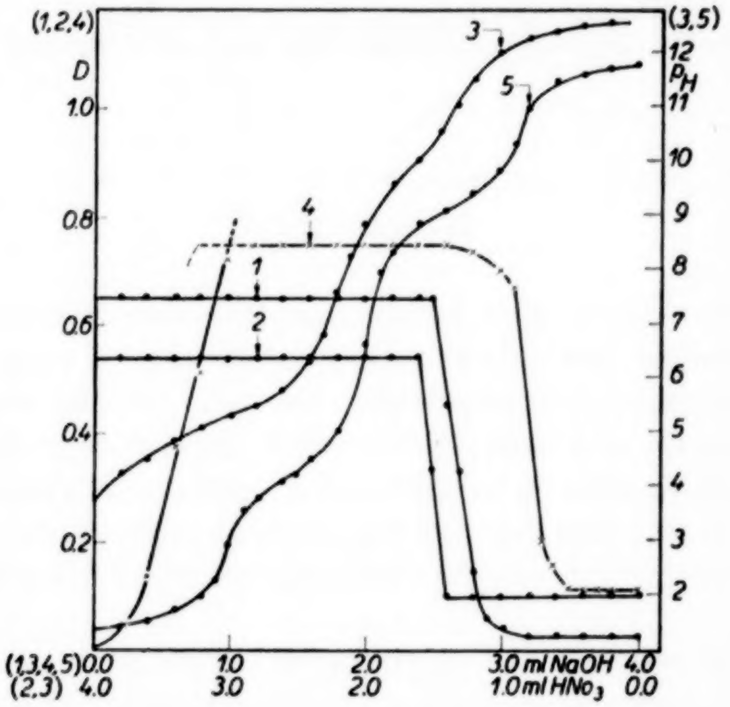

Fig. 1.

1. 3 ml 0.005 M $CuSO_4$ + 3 ml 0.2 N CH_3COOH + 3 ml 0.2 N H_3BO_3 + 5 ml 0.01 M salicylaldoxime + 6 ml H_2O + x ml 0.4 N NaOH.
2. 3 ml 0.005 M $CuSO_4$ + 3 ml 0.2 N CH_3COOH + 3 ml 0.2 N H_3BO_3 + 5 ml 0.01 M salicylaldoxime + 8 ml 0.2 N NaOH + 1 ml H_2O + x ml 0.4 N HNO_3.
3. pH-titration curve of exps. 1 and 2.
4. 3 ml 0.005 M $CuSO_4$ + 1 ml N HNO_3 + 1 ml N CH_3COOH + 2 ml M NH_4NO_3 + 4 ml 0.01 M salicylaldoxime + 9 ml H_2O + x ml N NaOH.
5. pH-titration curve of exp. 4.

Blue filter.

Curve 2 presents the heterometric curve obtained when the titration was begun at a high pH. The initial precipitation occurs at pH ∿ 10.7 and is complete at 10.1. The point at which dissolution begins coincides with the first point of complete precipitation and is equal to pH 10.1-10.3. Between pH's 10-11 the precipitation is incomplete. It is interesting to compare these results with those obtained in exp. 4. using NH_3-NH_4NO_3 as buffer (compare curves 4 and 5) from which it can be seen that the initial precipitation occurs at pH ∿ 1.5 and is complete at pH ∿ 3.0. From this pH till pH ∿ 9.5 the precipitate remains unchanged. At higher pH's the precipitate is redissolved. The difference between the results of curves 1 and 4 may be caused by interference of NH_3 in the high pH-regions. The results with boric acid buffer are more reliable.

Summarising, it may be said that a complete precipitation of CuR_2 occurs in the pH-region of 3-10.

The effect of acidity on metal complex binders

A heterometric titration was carried out in the presence of sulfuric acid. In 0.1*M* solution no precipitate occurred. In 0.01*M* solution (exp. 1a.) a maximum density value was obtained which was similar to the value obtained in 0.1*M* acetic acid (exp. 1). The point of initial precipitation was obtained in the presence of 0.01*M* sulfuric acid only after the addition of more than 30% of titrant. In contrast to this, precipitation occurred at once in acetic acid solution. In the sulfuric acid solution therefore the solubility of copper was much higher. In the presence of acetic acid we had the advantage of being able to use masking agents (exps. 5 and 6). In 0.01*M* sulfuric acid solution copper oxinate is soluble to an extent of $\sim 0.5 \cdot 10^{-4}$ mol per liter. The solubility in 0.1*M* acetic acid solution was about ten times lower. As experiments 4 and 7 show, buffered citrate or tartrate solutions could be used. Similar results were obtained with citrate or tartrate in acetic acid solution (exps. 5 and 6). In the presence of ethylenediaminetetraacetate copper could not be precipitated whatever the pH.

Determination in the presence of bivalent metals

Experiments 8-15 of Table I and Fig. 2 (the same experimental numbers are used in both cases) show the results of such titrations. Except in the presence of barium, there was no difficulty in the determination of copper and the error was generally 1-2% or 1-2 γ per ml. In the presence of barium the end-point of the titration was shifted and the error was high (exp. 9). The error could probably be eliminated at lower barium concentrations. The titrations lasted 10-20 minutes.

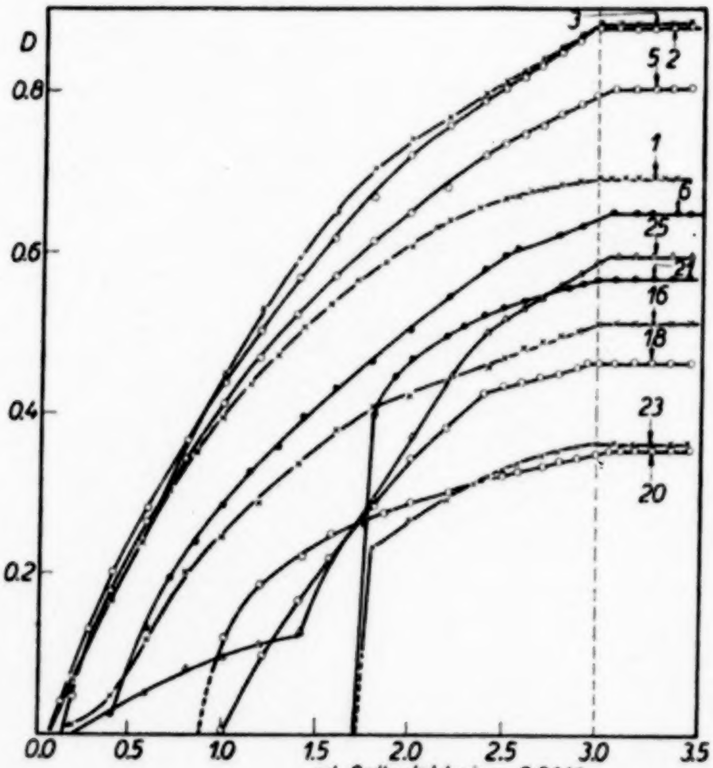

Fig. 2

Determination in the presence of bivalent metals

Clear end-points were obtained only in the presence of metal complex-binders. The highest concentration of foreign metal which could be present without interference was in the case of aluminium 0.1*M* and in the case of chromium or iron 0.05*M*. In the presence of aluminium

TABLE I

GENERAL COMPOSITION: 5 ml $CuSO_4$ 0.003*M* + 5 ml supplements + *x* ml salicylaldoxime 0.01*M*.
Content: 0.9536 mg Cu (= 3 ml salicylaldoxime). Filter: blue. Temp. = 20 °C

Exp. number	*Supplements*	*% Cu*	*Beginning of precip. at ml*	*Max. optic. density value*	*x = ml found*	*Approx. titration time in min*	*Error*		
							%	*γ*	*γ/ml*
1	1 ml CH_3COOH *M* + 4 ml H_2O	100	0.1	0.71	3.0	15	0.0	0.0	0.0
1a	1 ,, H_2SO_4 + 4 ,, H_2O		1.1	0.70		10			
2	2 ,, Na_2-tartrate *M* + 3 ,, ,,	100	0.1	0.88	3.0	11	0.0	0.0	0.0
3	2 ,, Na_3-citrate *M* + 3 ,, ,,	100	0.1	0.87	3.0	12	0.0	0.0	0.0
4	2 ,, ,, + 1 ml HNO_3 0.5*M* + 2 ml H_2O	100	0.3	0.71	3.07	17	2.3	22	2.2
5	2 ,, Na_2-tartrate *M* + 1 ,, CH_3COOH *M* + 2 ,, ,,	100	0.1	0.88	2.97	12	—1.0	9.5	1.0
6	2 ,, Na_3-citrate *M* + 1 ,, ,, + 2 ,, ,,	100	0.4	0.65	2.98	33	—0.7	6.6	0.7
7	2 ,, Na_2-tartrate *M* + 1 ,, HNO_3 0.5*M* + 3 ,, ,,	100	0.1	0.76	2.96	13	—1.3	12.3	1.2
8	2 ,, $MgSO_4$ *M* + 1 ,, CH_3COOH *M* + 2 ,, ,,	2.0	0.1	0.75	3.06	17	2.0	19	1.9
9	2 ,, $BaCl_2$ *M* + 1 ,, ,, + 2 ,, ,,	0.36	0.3	0.73	3.3				
10	2 ,, $ZnSO_4$ *M* + 1 ,, ,, + 2 ,, ,,	0.76	0.2	0.75	2.96	20	—1.3	12.3	1.2
11	2 ,, $MnCl_2$ *M* + 1 ,, ,, + 2 ,, ,,	0.91	0.3	0.72	2.97	15	—1.0	9.5	1.0
12	2 ,, $NiCl_2$ *M* + 1 ,, ,, + 2 ,, ,,	0.85	0.2	0.63	2.95	21	—1.7	16	1.6
13	2 ,, $Co(NO_3)_2$ *M* + 1 ,, ,, + 2 ,, ,,	0.84	0.3	0.78	3.00	12	0.0	0.0	0.0
14	2 ,, $CdSO_4$ *M* + 1 ,, ,, + 2 ,, ,,	0.45	0.3	0.75	3.06	15	2.0	19	1.9
15	2 ,, $Pb(NO_3)_2$ *M* + 1 ,, ,, + 2 ,, ,,	0.24	0.5	0.64	3.05	21	1.7	16	1.6
16	1 ,, $AlCl_3$ *M* + 1 ,, ,, + 2 ml Na_3-tartrate *M* + 1 ml H_2O	3.6	0.2	0.51	3.03	30	1.0	9.5	1.0
17	1 ,, ,, + 2 ,, ,, + 2 ,, ,,		0.6	0.62	3.05	23	1.7	16	1.6
18	1 ,, ,, 0.5*M* + 1 ,, ,, + 2 ,, Na_3-citrate *M* + 1 ,, ,,	6.9	1.1	0.46	3.02	17	0.7	6.6	0.7
19	1 ,, ,, ,, + 1 ,, ,, + 2 ,, ,, + 1 ,, ,,		1.1	0.46	3.02	17	0.7	6.6	0.7
20	1 ,, $Cr(NO_3)_3$,, + 2 ,, ,, + 2 ,, ,, *	3.7	1.0	0.35	3.07	16	2.3	22	2.2
21	1 ,, ,, ,, + 2 ,, Na_2-tartrate *M* + 2 ,, ,, *		1.7	0.57	3.10	14	3.3	28	2.8
22	1 ,, ,, ,, + 1 ,, ,, + 2 ,, ,, + 1 ,, ,, *		0.6	0.62	3.00	20	0.0	0.0	0.0
23	1 ,, ,, ,, + 1 ,, ,, + 2 ,, Na_3-citrate *M* + 1 ,, ,, *		1.8	0.36	3.00	19	0.0	0.0	0.0
24	1 ,, $FeCl_3$,, + 2 ,, Na_2-tartrate *M* + 2 ,, ,, **	3.5	0.3	0.74	∞	19			
25	1 ,, ,, ,, + 2 ,, Na_3-citrate *M* + 2 ,, ,, **		0.4	0.56	3.07	13	2.3	22	2.2
26	1 ,, ,, ,, + 1 ,, ,, + 2 ,, Na_2-tartrate *M* + 1 ,, ,, **		0.2	0.54	∞	21			
27	1 ,, ,, ,, + 1 ,, ,, + 2 ,, Na_3-citrate *M* + 1 ,, ,, **		0.6	0.45	3.04	21	1.3	12	1.2

* green filter ** red filter

(exps. 16-19) or chromium (exps. 20-23) either neutral or acid citrate or tartrate solutions could be added. Citrate probably reduces the maximum density values. The titration time was increased in the presence of acetic acid aluminium tartrate. In the presence of iron, better results were obtained if a red filter was used (exps. 24-27). The tartrate solutions gave no end-points and therefore only citrate solutions could be used. The titration time was generally 15-20 minutes and the error was 0.3%. The concentration of copper amounted in all cases to less than 10%. A factor which must be taken into consideration is the point at which initial precipitation occurs. The more titrant added before precipitation occurs, the more soluble is the analysed compound apparently, and the more restricted becomes the determination. From our results we learned that in the presence of aluminium or chromium, the use of tartrate is generally to be preferred. On the other hand, the point of initial precipitation was close to the beginning in the presence of iron citrate (exps. 25 and 27). In the above experiments which were carried out either in neutral or acidic solutions, the composition of the insoluble compound obtained was CuR_2.

SUMMARY

1. The initial precipitation of copper-salicylaldoxime occurs at pH ∿ 1.5. Between pH 1.5 and 3.0, the precipitation is incomplete. A complete precipitation occurs in the pH-region of 3-10. Between pH 10.1 and 10.7 the precipitate redissolves. At higher pH's a clear solution is obtained.

2. The solubility of copper salicylaldoximate is about ten times greater in 0.01 *M* sulfuric acid (∿$0.5 \cdot 10^{-4}$ mol) than in 0.1 *M* acetic acid.

3. In 10 ml of 0.1 *M* acetic acid solution in the presence of ∿ 99% foreign bivalent metals, one mg copper could be determined heterometrically with an error of 1-2%.

4. In the presence of ∿ 95% aluminium or chromium, either citrate or tartrate (0.2 *M*) were used as masking agents. In the presence of iron (∿ 95%), clear end-points were obtained only with citrate. One mg of copper could be determined with an error of 0-3%.

5. Whichever pH is used, copper is not precipitated in the presence of ethylenediaminetetraacetate.

RÉSUMÉ

1. La précipitation du cuivre-salicylaldoxime commence au pH ∿ 1.5. Entre les pH 1.5 et 3.0, la précipitation est incomplète; elle est quantitative du pH 3 au pH 10. Entre les pH 10.1 et 10.7 le précipité se redissout. Aux pH plus élevés on obtient une solution limpide.

2. La solubilité du cuivre-salicylaldoxime est environ dix fois plus grande dans l'acide sulfurique 0.01 *M* (∿ $0.5 \cdot 10^{-4}$ *M*) que dans l'acide acétique 0.1 *M*.

3. Dans 10 ml de solution d'acide acétique 0.1 *M*, on peut doser 1 mg de cuivre par hétérométrie avec une erreur de 1-2% (en présence d'environ 99% de métaux bivalents étrangers.

4. En présence de ∿ 95% d'aluminium ou de chrome, soit le citrate, soit le tartrate peut être utilisé comme agent de masquage. En présence de fer (∿ 95%) on n'obtient des points d'équivalence nets qu'avec le citrate. 1 mg de cuivre peut être dosé avec une erreur de 0-3%.

5. Le cuivre ne précipite pas en présence d'éthylènediaminotétraacétate, quel que soit le pH.

ZUSAMMENFASSUNG

1. Der Beginn der Fällung von Kupfer-Salicylaldoxim geschieht bei pH ∿ 1.5. Die Fällung ist im pH-Gebiet 1.5-3.0 unvollständig. Sie ist vollständig im pH-Gebiet 3-10. Zwischen pH 10.1-10.7 findet Auflösung statt und in höherem pH-Gebiet wird eine klare Lösung erhalten.

2. Die Löslichkeit von Kupfer-Salicylaldoxim ist 10 mal höher in 0.01 *M* Schwefelsäure als in 0.1 *M* Essigsäure.

3. 1 mg Kupfer kann in Gegenwart von ∿ 99% an Fremdmetallen in einer 0.1 *M* essigsäuren Lösung mit einem Fehler von 1-2% bestimmt werden.

4. In Gegenwart von ∿ 95% Aluminium oder Chrom wird Citrat oder Tartrat zur Maskierung verwendet. In Gegenwart von Eisen (∿ 95%) wird ein klarer Endpunkt nur in Gegenwart von Citrat erreicht. 1 mg Kupfer kann mit 0-3% Fehler bestimmt werden.

5. Die Fällung von Kupfer wird in Gegenwart von Äthylendiamintetraacetat verhindert unabhängig vom pH.

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RATIONALE OF THE RHODAMINE B METHOD FOR ANTIMONY

by

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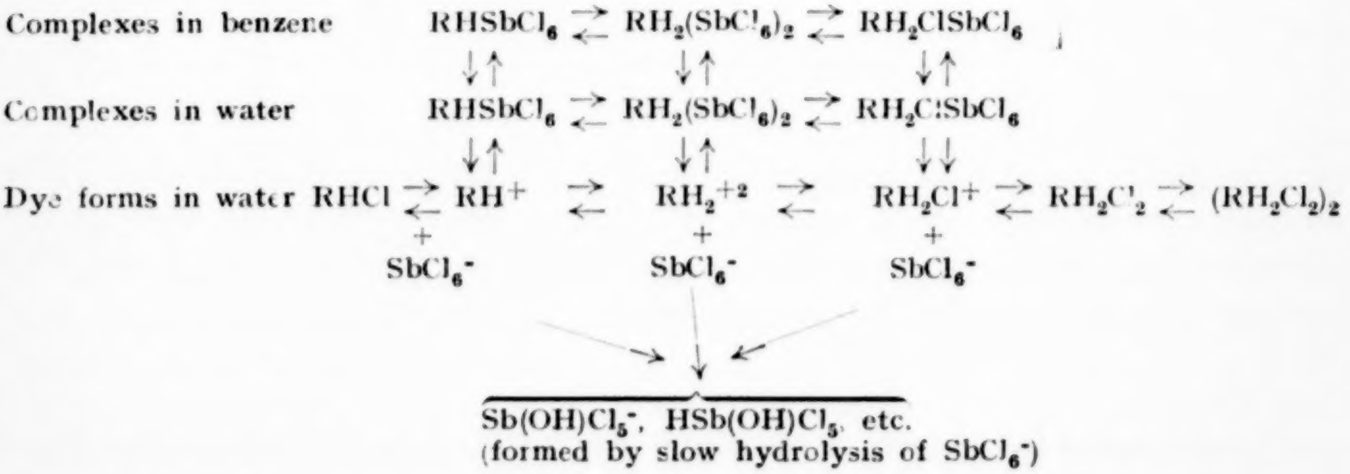
At the present time rhodamine B is generally considered to be the best reagent for the colorimetric determination of traces of antimony. The procedure in common use is based on the benzene extraction of rhodamine B chloroantimonate from aqueous solution. We are largely indebted to WEBSTER AND FAIRHALL[1] for establishing the best conditions for carrying out this determination. In brief, their directions call for oxidation of antimony (III) to antimony (V) in $6M$ hydrochloric acid with ceric sulfate, destruction of excess cerium (IV) with hydroxylamine hydrochloride, addition of rhodamine B and benzene extraction of the red-violet antimony complex.

The purpose of the present note is to discuss the chemistry underlying the procedure developed empirically by WEBSTER AND FAIRHALL and to point out some slight changes that may at times be worth while when the highest precision is sought.

A study[2] of the equilibria existing in hydrochloric acid solutions of rhodamine B has shown that the ions RH^+, RH_2^{+2} and RH_2Cl^+ (R = rhodamine B) are present together with some molecular species listed in the equilibrium diagram below. From the analytical standpoint the three dye cations are of chief importance because they can combine with chloroantimonate ion to form the insoluble, benzene-extractable, products $RHSbCl_6$, $RH_2(SbCl_6)_2$, and $RH_2ClSbCl_6$. In $6M$ hydrochloric acid the chief product is the violet salt $RHSbCl_6$, which can be isolated in fairly pure form by precipitation; this is in agreement with KUZNETSOV[3], who reported the formation of this salt. However, small amounts of the orange salts $RH_2(SbCl_6)_2$ and $RH_2ClSbCl_6$ are also formed, especially in hydrochloric acid solutions stronger than $6M$. When concentrated hydrochloric acid solutions containing respectively 0.2 millimole $SbCl_6^-$ and 0.1 millimole rhodamine B in 10 ml are mixed, an orange precipitate is obtained which is a mixture of the two salts mentioned.

Accordingly we have the following species in the hydrochloric acid-benzene system containing antimony (V) and rhodamine B:



The crucial step in the rhodamine B method is the conversion of antimony (III) to $SbCl_6^-$. A high concentration of hydrochloric acid, not less than 6*M*, is required for substantially complete transformation of trivalent antimony into this ion in the oxidation step. Cerium (IV) is one of the few suitable oxidizing agents. Permanganate, dichromate, bromine and hypochlorite all oxidize antimony less completely than ceric sulfate to $SbCl_6^-$. Oxidation by cerium (IV) is very rapid at room temperature and only a slight excess is needed. As long as no other oxidizable substances are present, less than the 0.5 millimole excess specified by WEBSTER AND FAIRHALL suffices. WARD AND LAKIN[4] have pointed out the importance of keeping the solution cool ($\lesssim$ 25° C). Hydroxylamine hydrochloride is entirely suitable for destroying excess cerium (IV), which otherwise would oxidize rhodamine B to a product coloring the benzene phase. It does not reduce antimony (V) at room temperature in 6*M* hydrochloric acid. If only a slight excess of cerium (IV) is added, it is not necessary to blow air into the separatory funnel to remove any chlorine above the solution.

As soon as $SbCl_6^-$ has been formed it begins to hydrolyze to $Sb(OH)Cl_5^-$ (which then hydrolyzes to other forms)[2,5]. In 6*M* hydrochloric acid at 25° the rate of hydrolysis is about 1% per minute. Since the hydrolysis product does not react with rhodamine B, it is imperative to add the reagent very soon after oxidation and, moreover, to time the interval if it is more than a fraction of a minute. The hydrolysis of chloroantimonate proceeds more slowly at lower hydrochloric acid concentrations, possibly because the species reacting with water is $HSbCl_6$ and not $SbCl_6^-$. In 2.0 and 3.8*M* hydrochloric acid the rate constants for the hydrolysis are respectively $2.7 \cdot 10^{-3}$ and $4.3 \cdot 10^{-3}$ min^{-1}, as compared to $9.6 \cdot 10^{-3}$ min^{-1} in 6.1*M* hydrochloric acid (25°).

The extraction coefficient for antimony

$$E = \Sigma\,[Sb]_{benzene} / \Sigma\,[Sb]_{H_2O}$$

is a function of the acidity and the excess of rhodamine B. If the simplifying assumptions are made that antimony is present as $SbCl_6^-$ (this is at least the predominant species) in the aqueous phase and as $RHSbCl_6$ in the benzene phase, with RH^+ as the predominant dye cation, we have the relations:

$$K = ([RH+]\,[SbCl_6^-])/[RHSbCl_6]_{benzene}$$
$$E = [RHSbCl_6]_{benzene}/[SbCl_6^-],$$

from which it follows that

$$E = [RH^+]/K.$$

Because of the complex composition of rhodamine B solutions (diagram above) it is difficult to write $[RH^+]$ as a function of hydrogen ion concentration, chloride ion concentration, and total rhodamine B concentration. However, for a specified hydrogen ion and chloride ion concentration, we may write

$$E = [dye]/K',$$

where [dye] refers to the total rhodamine B concentration in the acid aqueous phase

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after extraction. Fig. 1 shows that E increases linearly with [dye] in the range tested in $6M$ hydrochloric acid.

As the hydrochloric acid concentration is increased, the extractability of antimony falls off, chiefly because of the decrease in the concentration of RH^+. Fig. 2 shows the fraction of antimony (V) extracted into an equal volume of benzene from hydrochloric acid solutions of various strengths at a rhodamine B concentration of $4 \cdot 10^{-4}M$.

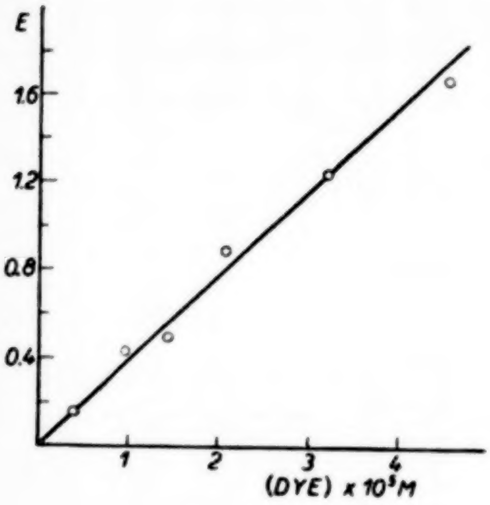

Fig. 1

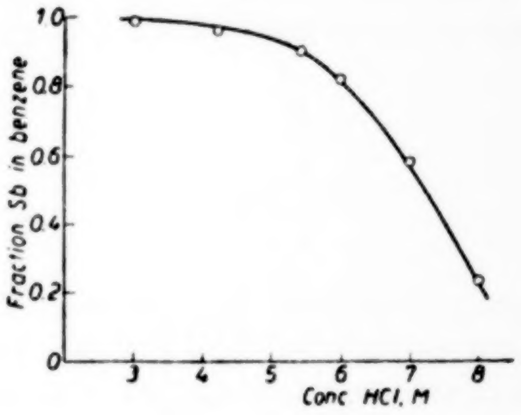

Fig. 2

Fig. 1. Extraction coefficient (benzene/aqueous phase, of antimony in the antimony (V) — rhodamine B system as a function of the dye concentration in the aqueous phase ($6M$ hydrochloric acid).

Fig. 2. Effect of hydrochloric acid concentration on extraction of rhodamine B chloroantimonate by benzene. Rhodamine B concentration $4 \cdot 10^{-4}M$; equal volumes of phases.

The antimony (V) solutions were obtained by diluting a stock solution in concentrated hydrochloric acid, in which hydrolyzed species are not present. In $6M$ hydrochloric acid, roughly 10% of the antimony is extracted as the orange complex $RH_2(SbCl_6)_2$, based on the observation that the molar ratio Sb/rhodamine B in the benzene is 1.05. A small, but unknown, quantity of $RH_2ClSbCl_6$ may also be present. The amounts of extracted $RH_2(SbCl_6)_2$ and $RH_2ClSbCl_6$ increase in hydrochloric acid solutions stronger than $6M$, but they do not compensate for the decreased extraction of $RHSbCl_6$, so that the total fraction of antimony extracted decreases with increasing acidity.

It is advantageous to carry out the extraction at an acidity lower than $6M$, say at $3M$, both because the extraction is then more complete and the rate of hydrolysis is less. The greater extractability below $6M$ acid has already been pointed out by WEBSTER AND FAIRHALL without explanation. Since a hydrochloric acid concentration of $6M$ is required for satisfactory oxidation of antimony, reduction of the acidity must be carried out by dilution with water immediately after this step. The reproducibility of such a procedure remains to be tested.

More complete extraction can also be obtained by increasing the rhodamine B concentration above the $2 \cdot 10^{-4}M$ used by WEBSTER AND FAIRHALL. The blank extract remains virtually colorless, even if the reagent concentration is increased to $2 \cdot 10^{-3}M$, provided the acidity is greater than $3M$. Below approximately $3M$ hydrochloric acid, the benzene extract of a blank begins to become colored violet because of increasing extraction of the colorless lactone form of the dye, which on standing is slowly converted to the colored form (RH^+Cl^-) as a consequence of the presence of hydrochloric acid in the benzene. The more favorable extraction coefficient resulting from decreasing the acidity or increasing the rhodamine B concentration would be of significance if the volume of benzene is relatively small compared to that of water. It would not be of importance if the two phases have equal volumes.

Finally, it should be pointed out that other metals reacting with rhodamine B may interfere more, or less, or about as much in 3*M* as in 6*M* hydrochloric acid. Qualitative observations on the strength of color imparted to 10 ml of benzene by 1 mg of metal are as follows:

	3*M* HCl	6*M* HCl
Hg (II)	strong	none
Au (III)	strong	weak
Cu (II)	none	none
Fe (III)	strong	strong
Ga (III)	weak	strong
Tl (III)	strong	strong

It may be said in conclusion that the original directions of WEBSTER AND FAIRHALL serve very well in most work, but at times the slight modifications suggested above may be advantageous.

SUMMARY

The chemistry of the colorimetric rhodamine B-benzene extraction method for the determination of antimony is examined and sources of error are considered.

RÉSUMÉ

La méthode de dosage colorimétrique de l'antimoine, au moyen de la rhodamine B, par extraction dans le benzène est examinée ainsi que ses sources d'erreurs.

ZUSAMMENFASSUNG

Die Methode der kolorimetrischen Bestimmung von Antimon mit Rhodamin B mittels einer Extraktion in Benzol wurde studiert, sowie auch ihre Fehlerquellen.

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THE ELECTROLYTIC SEPARATION FROM THORIUM NITRATE OF THORIUM C (^{212}Bi) AND THORIUM B (^{212}Pb) IN CHLORIDE SOLUTION

by

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INTRODUCTION

The quantitative electrodeposition of macro quantities of lead and bismuth and their separation from each other in both chloride and nitrate solutions by controlling the cathode potential is well established[1,2,3]. The solutions employed in the electrodeposition of micro quantities of metals are, in general, the same as those used on the macro scale. The separation of bismuth and lead by a micro electrolytic method was described by LINDSEY AND SAND[4], and ASHLEY[5] has reviewed the electrodeposition of very small quantities (of the order of $10^{-7}M$) of certain metals. The present paper describes the electrodeposition and separation of ThC and ThB from thorium nitrate in amounts capable of being detected only by their activity but using electrolytes similar to those referred to above[1,2,3,4].

The method is suitable for submicro preparation of these radio elements and also for their approximate determination.

From a consideration of its position among the electrochemically base metals, thorium would not be expected to deposit from aqueous solutions except perhaps as a hydrated oxide at the cathode under suitable conditions of hydrogen ion concentration. In cases where metals or their oxides can be electrodeposited, the depositions can be performed quickly and provide a means of preparing material for use as tracers in, for example, polarographic or analytical investigations, or for preparing films so thin that self-absorption effects are negligible.

One of the main differences in the technique required for gravimetric electrodeposits as opposed to radiochemical electrodeposits is that of cathode and cell design. The shape of the cathode has to conform to the geometry of the electrolytic cell as well as that of the castle of the Geiger Müller counter. In this connection, HULL[6] has stated that "one of the most important factors in attaining a high degree of accuracy in an electrodeposition method is the preparation of the sample in a thin, uniform film on a metallic base, such as a platinum disc". The films should be smooth, shiny and adherent.

APPARATUS

As the radioactive deposit is usually required on one face only of the electrode, the other face has to be stopped off using a non-conducting lacquer, or the cathode must be mounted permanently so that deposition can occur on one face only.

Several types of electrode were tested before the demountable polythene-backed cathode described below was adopted. A rotating cathode in which the nickel source dish was mounted horizontally by means of a plastic gland nut was unsatisfactory because, except at unmanageably high speeds, a large bubble of gas collected on the under side of the cathode. Using a similar mounting in which the source dish was vertical but stationary, electrolyte tended to collect in the small gap at the back of the cathode. A cathode holder made like a casette was not sufficiently watertight to prevent deposits being thrown onto the face of the cathode remote from the anode. Nickel discs or source dishes with a small tag for insertion into a rubber-covered platinum contact had to be stopped off with a lacquer, but this tended to peel during electrolysis in hot acid solutions.

The most satisfactory cathode mounting and the one used for the majority of the experiments was one in which the platinum or nickel cathode was embedded in polythene, leaving only a contact and one face exposed. These mountings were easily cleaned in hot hydrochloric acid and tests showed that they did not absorb any activity, neither was any count (other than the background) obtained after cleaning. These demountable cathodes were made as follows:

A platinum or nickel circular cathode about 14 mm diameter was cut out from foil and a 0.5 mm diameter wire about 15 mm long welded to a point on the periphery. The metal was degreased and cleaned in hot hydrochloric acid. In the case of the nickel, this cleaning etched the surface, but where platinum was used, it was first roughened slightly by lightly rubbing with fine emery. A disc of polythene approximately 20 mm in diameter × 2 mm thick was placed on a clean, smooth, flat metal surface heated by a small bunsen flame. When the polythene was sufficiently fluid (but still viscous) and began to change from opaque to transparent the metal disc was pressed into the centre of the polythene and some excess polythene squeezed up and over the edge of the metal disc, without trapping air bubbles. Final forming was effected by a piece of heated smooth steel. A 10 mm length of 3 mm bore polythene tubing was placed over the wire and sealed on to the polythene disc at one end, using the piece of heated smooth steel to form the weld.

The exposed tag of wire was used to make contact with the cathode lead-in wire, using a rubber tubing seal as shown in Fig. 1.

The anode was a 6-turn spiral made from about 60 mm of 0.5 mm diameter platinum wire sealed into a glass tube carrying a lead-in copper wire.

The electrolytic cell consisted of a 50 ml tall-form beaker clamped in position in a water bath heated by a hot-plate. It was stirred by a glass rod of approximately 3 mm diameter flattened and turned at the end to form a blade. HAISSINSKY[7] also prefers mechanical stirring to gas stream stirring because of possible contamination of the atmosphere with consequent increase in the background count. A two-pronged "paxolin" fork carrying the anode and cathode was placed round the cell, as shown in the figure.

The direct current was supplied from a transformer and rectifier unit with coarse and fine adjustment resistances in the circuit. The current was measured by means of a 2-range milliammeter.

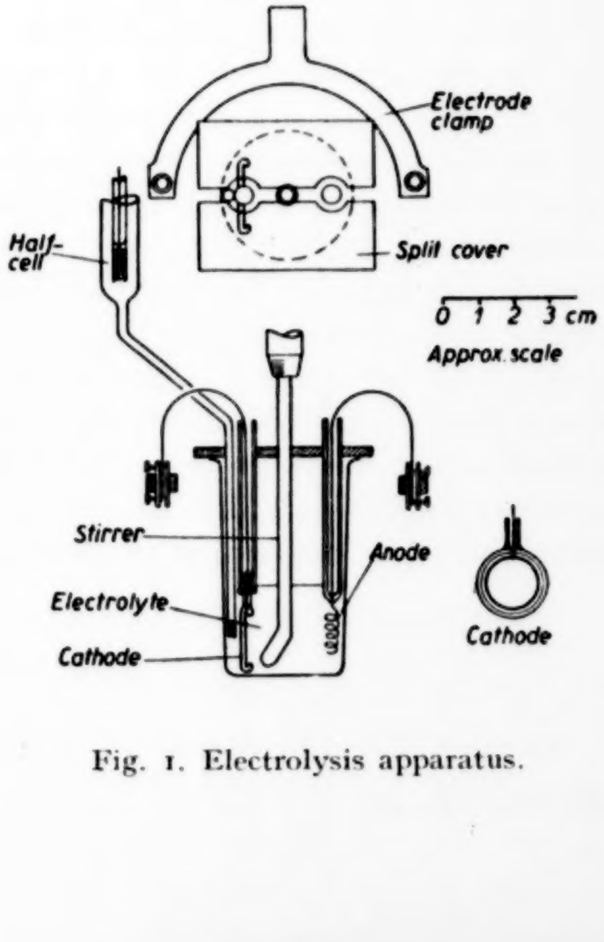

Fig. 1. Electrolysis apparatus.

The potential between the cathode and saturated calomel half-cell was measured by means of a potentiometer, the half-cell being placed as usual outside the current lines in the electrolyte. A saturated solution of potassium chloride was used for the bridge connection between the half-cell and electrolyte.

PREPARATION OF ELECTROLYTE AND PROCEDURE

From an "old sample" of thorium nitrate, $Th(NO_3)_4.4H_2O$, (one in which the preparation has been made for a sufficient time for equilibrium to be established among the radioactive daughters of thorium), 1 g was weighed out and dissolved in 20 to 25 ml 0.5*N* hydrochloric acid. The requisite amount of standard lead solution ('Analar' lead nitrate) and standard bismuth solution ('Analar' bismuth nitrate) was pipetted into the electrolysis solution which was heated in the water bath to a temperature of 80-90 °C. The clean electrodes and calomel half-cell were inserted and the electrolysing current and stirrer switched on. The current was increased in order to obtain the desired auxiliary potential. A split cover glass was placed over the cell and towards the end of the electrolysis period (usually up to 25 minutes) the underside of the cover glass and walls of the beaker were rinsed down by a jet of distilled water.

At the end of the deposition time, the cathode with the deposit of ThC was withdrawn while the current was still on, washed with distilled water and then alcohol and dried before placing in the lead castle of the counting apparatus.

To check for completion of deposition another cathode could be inserted and electrolysis continued for a further period of time.

After the ThC had been removed, ThB could then be deposited on a fresh cathode using a current of about 250 milliamp, no controlled cathode potential being employed.

The activity of the deposits in counts per minute after correction for background and lost counts was plotted against the time. Since the process of radioactive decay proceeds according to a logarithmic law, a plot of activity on the logarithmic scale of semi-log paper against time, using the linear scale, is a straight line. The slope of this line determines the half-life of the radiodeposit. The half-life thus determined confirmed the presence of the particular isotope and its purity. Thus, if some of the ThB (lead) was co-deposited with the ThC (bismuth), it was observed that a higher, incorrect value for the half-life of the ThC was obtained.

In plotting the activity against the time on semi-log paper for ThB, it was observed that initially (for the first hour approximately) the activity increased. This was an example of transient equilibrium, the curve exhibiting growth of a daughter activity in the freshly purified parent fraction; it was followed by the normal decay curve of the parent, *viz.* ThB.

By allowing the solution of thorium nitrate to stand for a sufficient period of time after removal of the ThC and ThB, the radiochemical equilibrium was re-established and more ThC and ThB were produced. The period required was usually of the order of about 10 half-life periods but in some experiments a period of 1 week intervened before further "milking" of the thorium nitrate was effected.

CONCLUSIONS

The foregoing may be summarized as follows. The electroseparation of ThC and ThB from each other and thorium in chloride solution has been shown to be possible; the deposited ThC, so far as could be ascertained, is radiochemically pure.

In order to separate the two metals electrolytically, it is essential to employ the correct cathode potential and in order to do this, sufficient carrier must be added. Although deposition times of the order of 20 minutes were used, it is possible to obtain a deposit of high specific activity in less time if the metal is required as a tracer in subsequent work. Both platinum and nickel cathodes can be used.

Complete removal of ThC from the solution was not effected (this is discussed below).

The smallest weight of carrier added was 0.176 mg of bismuth.

If the cathode potential is too high, then ThC and ThB co-deposit and a decay curve that is predominantly that of ThB results.

An auxiliary potential of not more than 250 mV versus the saturated calomel half-cell and saturated potassium chloride is satisfactory.

TABLE I

TABLE OF EXPERIMENTAL CONDITIONS AND RESULTS

Expt. no.	Electrolyte composition				Current	Time	Temp.	Auxiliary potential V. satd. calomel	Material of:		Half-Life		Initial ThC activity (³) counts/
	$Th(NO_3)_4$	0.5N HCl	Carrier Bi	Carrier Pb					Cathode	Anode	ThC	ThB	
	g	ml	mg	mg	mA	min	°C	mV			min	h	min
1	1	20	1.76	—	4.0-6.0	25	80-90	280-263	Nickel	Platinum	60	—	
					250	15	80-90	—	Nickel	Platinum	—	11.5[1]	
2[2]	1	20	—	—	2.0-1.6	22	80-90	242	,,	,,	57	—	
3	1	20	1.76	—	4.1	4	90	205					
					5.0	16		230-220	,,	,,	62.5	—	
4	1	20	—	—	4.1	25	90-95	245-228	,,	,,	60	—	
5	1	20	—	—	4.1-4.4	25	80-90	260	,,	,,	60	—	
6	1	20	—	—	4.0-4.1	45	80-90	400 rising to 550	,,	,,	62.5	—	6000
7	1	20	0.176	—	4.1	32	80-90	260 rising to 600	,,	,,	62	—	4500
8	1	20	—	—	4.1-4.5	25	80-90	520-650	,,	,,	80[4]	—	
9	1	20	1.76	—	4.0-4.1	25	80-90	240-257	Platinum	,,	60	—	4250
10	1	20	—	1.77	4.1	25	80-90	800-670[5]	,,	,,	—	—	8800[6]
					250	20	80-90	-	,,	,,	—	—	155
11	1	25	1.76	—	4.1-3.95	25	80-90	252-240	,,	,,	60.6	—	7800
12	1	25	0.88	—	4.0-4.3	25	80-90	240-300	,,	,,	60.0	—	9800
					4.25-0.75	25	80-90	340-270	,,	,,	60.0	—	2600
13	1	25	0.88	—	4.3-4.4	25	80-90	230-330	,,	,,	60.0	—	9500
					4.5-0.7	21	80-90	250	,,	,,	60.0	—	2850
					1.2	4	80-90	300	,,	,,			
14	1	25	0.44	—	4.4-1.65	40	80-90	230-270	,,	,,	60.5	—	7900
					4.3-1.4	15	80-90	254-260	,,	,,	60	—	3000
15	1	25	0.44	—	4.3-4.1	15	80-90	230-260	,,	,,	63.5	—	4400
					4.4-1.8	25	80-90	242-270	,,	,,	55[7]	—	5600
16	1 +0.5g hydrazine sulphate.	25	0.44	—	4.3-1.0	25	80-90	240-250	,,	,,	60.5	—	6200

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[1] The determination of the half-life value for ThB needs several hours, but these readings were obtained from activity readings made late at night and completed the following morning, so that points in the mid part of the curve were missing. Thus this half-life value would be expected to be approximate only.

[2] Continuation of Experiment 1.

[3] These readings were made in the same counting apparatus under comparable conditions.

[4] Auxiliary potential too high.

[5] Due to error in potenticmeter setting.

[6] ThB and ThC co-deposited.

[7] Value found from initial readings of decay curve.

DISCUSSION

Any polonium (216Po, ThA) that might be deposited (polonium is electrochemically more noble than bismuth[8]) has a half-life of 0.158 sec and can be allowed to decay before plotting the half-life of ThC.

Theoretically, the ThC cannot be removed from solution completely because, apart from electrochemical considerations, as soon as equilibrium between ThC and ThB is disturbed by removal of some of the former, ThC is formed from ThB by ejection of a β particle from the nucleus of a ThB atom.

The ThC activity growing in the parent fraction ThB is responsible for the initial increase of activity of the ThB electrodeposits before the decay curve for the longer-lived parent (ThB) is subsequently obtained.

Experiment 14, compared with Experiment 12, indicates the effect of a longer electrodeposition time — the ThC already deposited on the cathode decays during the extra 20 minutes of electrolysis time.

When insufficient ThC or bismuth had been deposited on the platinum cathode, it was not possible to obtain the desired cathode potential. In one experiment, the calomel half-cell was initially 418 mV negative to the platinum cathode, but when the current was increased sufficiently to deposit some ThC and bismuth, the calomel half-cell became 200 mV positive to the cathode. An interval of approximately 2 minutes was required in Experiment 4 to obtain a reading of the auxiliary potential. If the amount of deposit is insufficient to form a monolayer, there is no satisfactory method for predicting the potential at which to carry out the electrolysis, as when using submicrogram amounts of material it is not at all unusual for the average depth of a deposit to be less than a monolayer[9].

It is possible to calculate the order of magnitude of the weight of ThC deposited, from the data obtained in Experiment 12. Taking for example a count per minute of 9800 for the initial activity of the ThC ($T\frac{1}{2}$ = 60.5 min mass 212) the order of magnitude can be arrived at as follows.

From FRIEDLANDER AND KENNEDY[10]:

λ = constant N = Avogadro Number W = weight of deposit in grams

$$\lambda = \frac{0.693}{60.5 \text{ min}} = \frac{0.693}{60.5 \times 60 \text{ sec}} = 1.91 \cdot 10^{-4} \text{ disintegrations/sec}$$

$$\frac{-dN}{dt} = \lambda N = \frac{\lambda W \times 6.02 \times 10^{23}}{212} \text{ disintegrations/sec}$$

$$= \frac{1.91 \times 6.02\, W \times 10^{19}}{212} \text{ disintegrations/sec}$$

$$= 5.42\, W \cdot 10^{17} \text{ disintegrations/sec}$$

It is necessary at this stage to assume the efficiency of the counter, which has been taken for the purposes of this calculation as 3.3%.

$$\text{Thus } \frac{-dN}{dt} \text{ taken as } \frac{9800 \times 30}{60} \text{ disintegrations/sec}$$
$$= 4900 \text{ d/sec}$$
$$\frac{-dN}{dt} = 4900 = 5.42\ W \cdot 10^{17}$$
$$W = 9 \cdot 10^{-15} \text{ g ThC.}$$

The equilibrium concentration of ThC in thorium nitrate can also be calculated. At equilibrium ThC is present in the proportion of its half-life (60.5 min) to that of ^{232}Th (half-life $1.39 \cdot 10^{10}$ years). Thus the concentration of ThC (^{212}Bi) is:

$$60.5 \times \frac{1}{1.39 \times 365 \times 24 \times 60 \times 10^{10}} = 8.29 \cdot 10^{-15}$$

Thus 1 g ^{232}Th is in equilibrium with $8.29 \cdot 10^{-15}$ gThC.
In 1 g $Th(NO_3)_4 4H_2O$(= 0.42 g ^{232}Th) there would be:

$$8.29 \times 0.42 \times 10^{-15} = 3.5 \cdot 10^{-15} \text{ gThC.}$$

The orders of magnitude are therefore approximately the same in the two cases.

SUMMARY

An electrodeposition process is described for separating thorium C and thorium B from radiochemically "old" samples of thorium nitrate in hot 0.5*N* hydrochloric acid solution. The thorium C is first deposited on either platinum or nickel cathodes of special design using a controlled potential at the cathode, followed by the deposition of thorium B. Weights of the order of 10^{-15} g ThC are involved.

RÉSUMÉ

Une méthode par électrolyse est décrite pour la séparation du thorium C et du thorium B d'échantillon "radiochimiquement vieux" de nitrate de thorium; on utilise des solutions chaudes dans l'acide chlorhydrique 0.5*N*. Le thorium C se dépose le premier sur des cathodes spéciales soit de platine, soit de nickel, à potentiel contrôlé. Des quantités de l'ordre de 10^{-15} g de ThC sont entraînées.

ZUSAMMENFASSUNG

Es wird eine elektrolytische Methode beschrieben, um das Thorium C und das Thorium B eines "radiochemisch alten" Musters von Thoriumnitrat abzutrennen. Man verwendet heisse Lösungen in Salzsäure 0.5*N*. Das Thorium C lagert sich als erstes an Spezialkathoden aus Platin oder Nickel bei kontrolliertem Potential ab. Es werden Quantitäten in der Grössenordnung von 10^{-15} g von Thorium C abgeschieden.

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COULOMETRIC TITRATION OF URANIUM WITH ELECTROGENERATED TITANOUS ION

by

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CARSON[3] described a method for the coulometric titration of uranium based on preliminary reduction from the +6 to the +4 state with a lead reductor and final titration of the +4 uranium with electrogenerated bromine in the presence of the ferrous-ferric couple as a catalyst. FURMAN, BRICKER AND DILTS[5] developed a similar method, except that solid cadmium amalgam was used for the preliminary reduction and electrogenerated ceric ion was used for the titration of the ferrous ion produced by adding excess ferric ion to the reduced uranium solution. These authors were interested in determining uranium in the low milligram and microgram range, and in view of the very small quantities the performance of both methods was quite satisfactory. It is possible that these methods could be adapted to macro amounts of uranium. However, direct titration of +6 uranium to the +4 state with an electrogenerated reductant is more attractive in principle because it entails fewer sources of error, and it is simpler in practice. In this study such a direct titration has been developed, using electrogenerated titanous ion as the reductant and potentiometric end-point detection.

The method is sufficiently accurate for critical uranium assays. In contrast to the volumetric method usually used, coulometric titration has the advantage in principle of being "absolute", in the sense that the result is obtained by direct measurement of the fundamental quantities *current* and *time*. Classical volumetric procedures are indirect since they depend on the use of standard substances, whose purity must, in turn, be established. Coulometric titration is also more advantageous in practice because precise measurements of current and time are more easily performed than volumetric measurements.

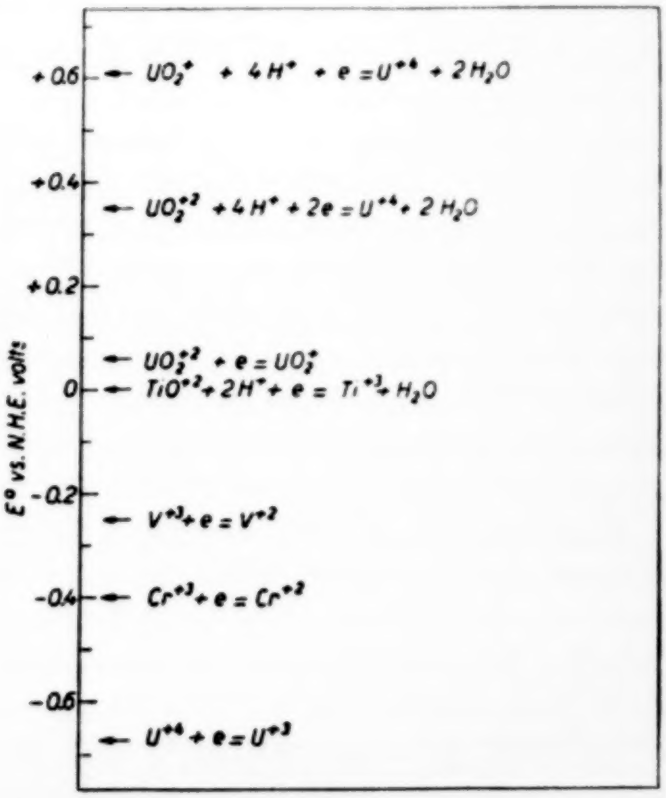

Fig. 1. Standard Potentials.

The standard potentials of the various uranium couples are represented in Fig. 1. The only feasible reduction for precise analytical purposes is from the +6 to the +4 state. The potential of the U^{+4}—U^{+3} couple is so strongly reducing that +3 uranium readily reduces hydrogen ion, and consequently the quantitative reduction of +4 uranium to the +3 state is impractically difficult in aqueous solutions. It is also evident that any reductant which is capable of reducing +6 uranium to the +5 state, in acid medium, will also be capable of reducing the latter to the +4 state. In strongly acid medium +5 uranium is incapable of stable existence because it rapidly disproportionates into the +4 and +6 states[7,8,9]. In weakly acid medium (pH about 2 to 4) the disproportionation of +5 uranium is sufficiently slow so that considerable concentrations of it can be produced, but even under optimum conditions the disproportionation rate is still great enough to preclude quantitative reduction of +6 uranium to the +5 state.

Since the UO_2^{+2}—U^{+4} couple involves four hydrogen ions its potential is greatly influenced by hydrogen ion concentration, but even in strongly acid medium the oxidation potential is not very large. Consequently reduction of +6 uranium requires a strong reductant. Three likely reductants are titanous, chromous, and vanadous ions, and the first two have been used for this purpose by the classical volumetric technique[4,6]. Chromous ion, with the greatest reducing potential (see Fig. 1), is the most favorable thermodynamically, but its electrogeneration with 100% current efficiency by reduction of chromic ion seems to be well-nigh impossible. FURMAN, BRICKER AND DILTS[5] were unable to obtain current efficiencies better than about 5% in the reduction of chromic ion at a platinum cathode, because of interference by hydrogen ion reduction. Using a mercury cathode Mr. A. M. HARTLEY in our laboratory observed a much better current efficiency, but even under most optimum conditions (minimal hydrogen ion concentration and non-complexing solutions) the highest value was only about 95%. The electrogeneration of vanadous ion by reduction of vanadic ion probably would be nearly as difficult as chromous ion. Consequently titanous ion is the logical choice for the coulometric titration of +6 uranium.

The use of electrogenerated titanous ion for coulometric titrations was originated by ARTHUR AND DONAHUE[1], who employed it for the titration of ferric iron in a titanyl chloride-hydrochloric acid medium. ARTHUR AND DONAHUE used a gold cathode, but we experienced difficulty obtaining precisely 100% current efficiency with it and turned to the use of a mercury cathode on which the overvoltage of hydrogen is so high that the precise generation of titanous ion is easily accomplished. PARSONS AND SEAMAN[12], in a paper published while this investigation was in progress, also reported difficulties with a gold cathode and used a mercury cathode for the titanometric determination of dyestuffs by the external generation technique.

Most recently, MALMSTADT[11] reported successful generation of titanous ion at both *platinum* and *titanium* cathodes from titanyl chloride-hydrochloric acid solutions when the concentration of hydrochloric acid was greater than $7M$. With smaller hydrochloric acid concentrations the current efficiency was less than 100%. In view of the close proximity of the Ti^{+4}—Ti^{+3} potential to that of hydrogen ion this is most remarkable. It means that the *formal* potential of the Ti^{+4}—Ti^{+3} couple in strong hydrochloric acid must be considerably greater (more oxidizing) than the potential at which hydrogen ion is reduced on platinum. MALMSTADT's results in the titration of

vanadium indicate a current efficiency within a few parts per thousand of 100%, but whether the generation is precise enough for critical assay purposes remains to be established.

EXPERIMENTAL

Titration cell. The titration cell, shown in Fig. 2, had a capacity of 200 ml and the total volume of solution was usually 75 ml. The mercury pool cathode (area *ca.* 8 cm^2) is held in the cupped depression in the bottom of the cell. Efficient stirring is provided by a magnetic stirrer, with the Teflon-coated stirring bar floating on the mercury surface.

A cadmium rod, in a 1M cadmium chloride solution, served as auxiliary electrode (anode). The sintered glass disk in the bottom of the anode compartment was of very fine porosity, and the level of the anolyte was maintained somewhat above that of the catholyte.

A bright platinum foil (1 × 1.5 cm) served as indicator electrode, and a saturated calomel electrode was used as the reference electrode.

The electric heating mantle, which also served to support the cell, was fabricated by winding asbestos-insulated resistance wire around a crystallizing dish.

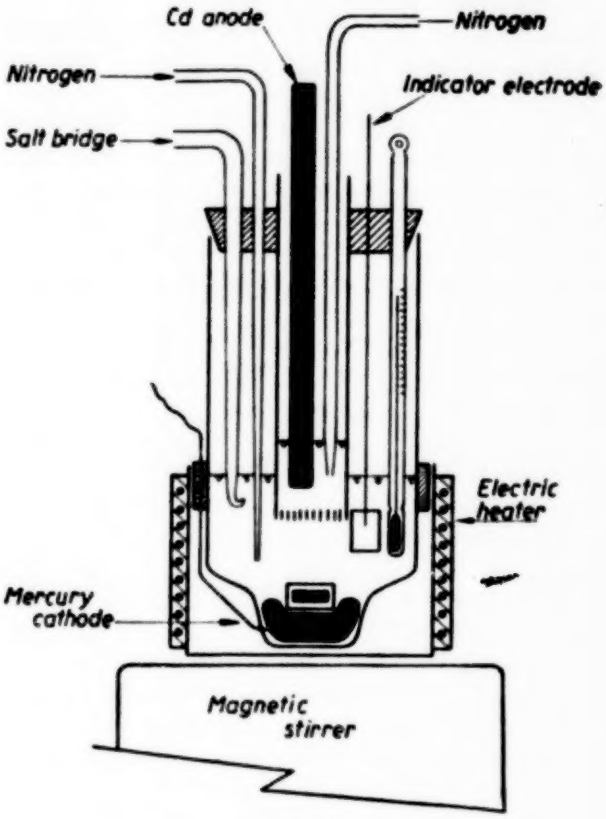

Fig. 2. Titration Cell.

Electrical instrumentation. The electrolysis current was automatically held constant to better than ±0.01%, by the instrument previously described[10]. The current was measured by observing the iR drop across a precision resistance in series with the cell with a Leeds and Northrup Type K potentiometer. The exact value of the measuring resistor was established to within ±0.005% by calibration against a certified resistance standard from the Leeds and Northrup Co. The Weston standard cell used with the potentiometer was calibrated against a certified Weston standard cell from Eppley Laboratories, Inc.. All electrical quantities are expressed in absolute units, on which scale the value of the faraday is 96,493 coulombs. The measuring resistor was selected so that the iR drop was of the order of 1 volt, and since the potentiometer readings were precise to ±0.01 mV, the overall error of current measurement was well within ±0.01%.

Time was measured with a Standard Electric Time Co., Model S-10, electric stopclock (range 1000 sec with 0.1 sec divisions). This clock is equipped with a solenoid brake, and the "start-stop" error per operation is not greater than ±0.01 sec. The accuracy — as distinct from precision — of this type of chronometer is dependent on the constancy of the frequency of the a.c. supply voltage. Since a frequency-regulated power supply was not available, the clock was driven from the public utility 110 V, 60 cycle, a.c. line. To minimize errors from the inevitable small variations in frequency the generating currents were selected so that titration times were relatively long (600-1200 sec).

We believe that time measurement was the chief uncertainty in the titrations. To obtain an estimate of the timing error introduced by frequency variations in the supply voltage, the reading of the clock was compared over 1200 sec intervals with the precise time signals broadcast by the National Bureau of Standards Station WWV. From several comparisons made at different times on different days, extreme deviations of as much as 0.2% were noted, but the average variation was close to ±0.05%.

Uranium standard. Known quantities of uranium for the titrations were obtained as follows. A sample of Merck uranyl acetate dihydrate (purest reagent grade) was recrystallized from dilute acetic acid, and stored in a hygrostat at a relative humidity of 57%. After several weeks the water content of the salt corresponded closely to the theoretical value. The exact composition was established by igniting 5 g samples to U_3O_8 in a platinum crucible in an electric muffle furnace at 950° to 1000 °C. Although exact information on the range of relative humidities over which uranyl acetate dihydrate is stable is not available, a relative humidity of 57% is believed to be within the stable range. However, the salt continued to lose weight at a very slow rate even after a composition corresponding to the dihydrate had been reached. The salt was assayed by ignition to U_3O_8 at biweekly intervals, so that the exact uranium content at each time of use was known.

By careful potentiometric titration of a 5 g sample of the salt in 1 M perchloric acid with 0.01 M ceric sulfate, and correction for a very small blank observed with the acid alone, the salt was found to contain 0.057 percent +4 uranium. Correction for this was applied when the salt was weighed out for the titrations.

The U_3O_8 could, of course, have been used for the titrations, but since its dissolution is less easy than that of the acetate it was more convenient to use the latter.

Individual samples of the uranyl acetate dihydrate for each titration were weighed on a microbalance with carefully calibrated weights, and bouyancy corrections were applied. The weighing error was not greater than ±0.005 mg, and since the weight of the samples was 50-200 mg, the uncertainty of the weighings was less than ±0.01%.

Titanic supporting electrolyte. For reasons discussed in a following section, a supporting electrolyte composed of *ca.* 0.08M +4 titanium, 0.2 to 1 M citrate, and adjusted to pH = 1, was selected as most satisfactory.

To ensure a small blank correction the supporting electrolyte must be as free as possible of oxidizing impurities, which means a very pure source of +4 titanium. Several possibilities were investigated, including titanyl sulfate, potassium titanyl oxalate, and titanium tetrachloride. The latter proved to be most satisfactory, and is commercially available in a high state of purity (Amend Drug and Chemical Co., New York).

Following essentially the same procedure recommended by ARTHUR AND DONAHUE[1], 200 ml of titanium tetrachloride was treated with water, in small portions (hood!), until the energetic hydrolysis ceased. The resulting pasty mass was then dissolved with more water and diluted to 500 ml. Analysis of the resulting clear solution showed it to be 3.35M in respect to titanium.

Stock solutions of supporting electrolyte were composited by mixing appropriate volumes of the titanyl chloride solution and pure citric acid solution. The pH was adjusted to the desired value by addition of sodium hydroxide or hydrochloric acid, and was measured with a glass electrode. These solutions were stable indefinitely when the pH was between 1 and 4.

Titration procedure. The sample of uranyl acetate dihydrate was transferred to the empty titration cell and dissolved in 25 ml of water. Fifty ml of the titanic-citrate supporting electrolyte was then added, the solution was deaerated with purified nitrogen, and heated to the desired temperature (usually 85 °C). Pure, dry mercury for the cathode was then introduced.

The electrolysis was then begun with the appropriate constant current and with a continuous stream of nitrogen passing through the solution. The potential of the platinum indicator electrode against a saturated calomel reference electrode was observed with a potentiometer. The titration was stopped when the potential of the indicator electrode reached the known value corresponding to the equivalence point. After subtracting the small blank correction *(vide infra)* from the total observed time, the weight of uranium found was computed from the relation

$$W = \frac{238.07\ it}{2 \times 96{,}493},$$

where t is the corrected titration time and i is the value of the generating current.

As the e.p. was approached the generating current was applied in small increments (*ca.* 0.5 sec) and the potential of the indicator electrode was allowed to become constant (±5 mV) between successive increments. Constant potential was attained very quickly until right at the e.p., when about 3 minutes was required. Sufficient readings were taken to define the course of the titration curve immediately before and after the e.p., and the exact e.p. was determined by interpolation.

Blank corrections were determined by performing titrations under exactly the same conditions except that no uranium was added. The blank correction was very small and reproducible, and needed to be determined only once for a particular batch of supporting electrolyte. With 50 ml of supporting electrolyte 0.08M in respect to titanium, it corresponded to only 0.009 mg of uranium with a total citrate concentration of 0.25M, and 0.035 mg with 1M total citrate.

The cathode mercury should not be added until air has been removed from the solution. When the mercury was added while air was present the blank correction increased and became somewhat erratic, presumably because the mercury was slowly oxidized by dissolved oxygen and the resulting mercurous and mercuric species were subsequently reduced by titanous ion. The mercury can be used repeatedly, provided that it is washed with water, dried, and filtered, between titrations. It is advisable to dispense the mercury into the cell from a container in which it has been stored under nitrogen. Apparently mercury in contact with air holds small amounts of oxygen on its surface, because when such mercury was used the blank correction was increased to a small but significant extent.

TITRATION CHARACTERISTICS AND PERFORMANCE DATA

The characteristics of the titration were studied in sulfuric and hydrochloric acid media — using titanyl sulfate and titanyl chloride as the sources of +4 titanium — and in oxalate and citrate media over a range of pH. Hydrochloric acid media are unsuitable because the +6 uranium is reduced by mercury in the presence of chloride[2], and the resulting mercurous and mercuric chlorides are reduced rather slowly by titanous ion. Sulfuric acid media are unsatisfactory because of the pronounced tendency of the +4 titanium to undergo hydrolytic precipitation; this can be minimized by using a relatively large concentration of sulfuric acid, but this in turn introduces some other difficulties. Oxalate media are unsatisfactory because of the uranium-catalyzed photodecomposition of the oxalate. Citrate media, composited as described above under EXPERIMENTAL proved to be most satisfactory. The +4 titanium is well complexed by citrate and the supporting electrolyte is stable indefinitely.

Titration curves in citrate media over a pH range from 1 to 4 are shown in Fig. 3. Although the titration can be performed up to a pH of about 4, a pH of 0.5 to 1.5 is essential for rapid attainment of equilibrium and most accurate results.

Between about pH 2 and 4 the overall reaction between the +3 titanium and the +6 uranium is quite slow, as evidenced by a slow attainment of potential equilibrium. Doubtless the overall reaction at any pH proceeds by two successive 1-electron reductions of the +6 uranium to the +5 and +4 states, and the reduction of U^{+5} to U^{+4} probably is the rate-determining step. From the study of KRAUS, NELSON AND JOHNSON[8] the U^{+5}-U^{+4} couple is known to function much less reversibly than the U^{+6}-U^{+5} couple, and +5 uranium has optimum stability over the pH range from about 2 to 4. From our experiments the optimum stability range in the presence of citrate does not appear to be much different than in non-complexing media, indicating that complexation with citrate is relatively weak.

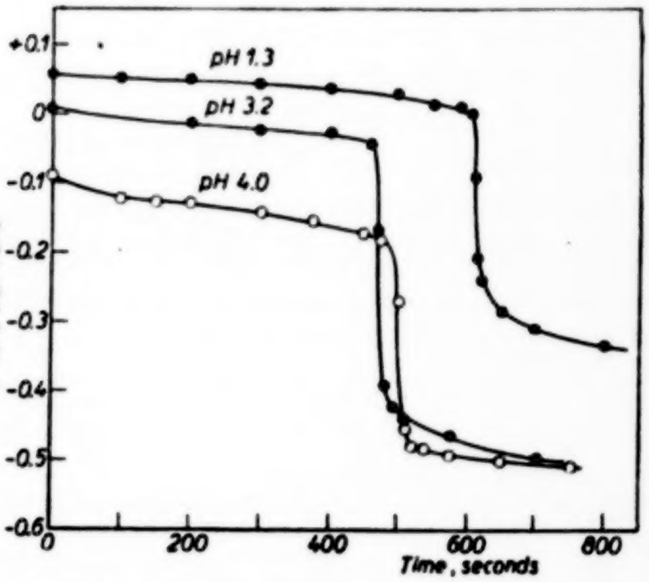

Fig. 3. Influence of pH on titration curve of +6 uranium. In each case the quantity of uranium titrated was *ca.* 25 mg, and the generating current was 39 milliamp.

The reduction of +6 uranium to the +5 state is rapid at all pH's, but at pH 3 to 4 the reduction of +5 uranium to the +4 state appears to be quite slow and is responsible for a slow attainment of equilibrium. This difficulty disappears when the pH is smaller than about 2.

Because the titration reaction

$$U^{+6} + 2Ti^{+3} = U^{+4} + 2Ti^{+4}$$

is assymetrical, coupled with the presence of a large excess of $+4$ titanium, the titration curve is not perfectly symetrical about the equivalence point, and the latter does not coincide exactly with the point of maximum slope. However, the rate of potential change is so great that the discrepancy is very small. Furthermore, by choosing the same potential for the actual and blank titrations as an arbitrary e.p. any slight discrepancy is cancelled out.

At pH = 1 the rate of change of potential at the e.p. is approximately 500 mV/sec with a 78 milliamp generating current, and is not much influenced by the uranium concentration or the concentration of citrate. Consequently, the e.p. can easily be established to well within 0.1 sec, which in a 1200 sec titration of 112 mg of uranium corresponds to an uncertainty of less than 0.008%.

Table 1 contains the results of nineteen trial titrations which demonstrate the accuracy of the method.

TABLE I

COULOMETRIC TITRATION OF $+6$ URANIUM WITH TITANOUS ION

In all cases the solution volume was 75 ml, the concentration of $+4$ titanium was 0.08*M* and the pH was 1.0-1.2. For 112 mg of uranium the generating current was *ca.* 78 milliamp and the titration time was about 1200 sec. For 28 mg of uranium the generation current and titration time were about 40 milliamp and 600 sec. Temperature was 85° C. In trials 1 to 11 the total citrate concentration was 0.27*M*; in trials 12 to 19 it was 1.0*M*.

Trial No.	*Uranium taken mg*	*Uranium found mg*	*Error %*
1	112.38	112.42	+0.04
2	112.40	112.33	—0.06
3	112.35	112.25	—0.09
4	112.37	112.30	—0.06
5	112.41	112.16	—0.22
6	112.47	112.50	+0.03
7	112.45	112.45	0.00
8	28.096	28.112	+0.06
9	28.110	28.196	+0.31
10	28.155	28.151	—0.01
11	28.110	28.118	+0.03
12	112.49	112.31	—0.16
13	112.46	112.39	—0.06
14	112.50	112.35	—0.13
15	112.45	112.48	+0.03
16	28.105	28.101	—0.01
17	28.113	28.140	+0.10
18	28.136	28.101	—0.12
19	28.139	28.118	—0.07
		Av.	—0.02 ± 0.08

The concentration of total citrate does not appear to be very critical, provided that it is at least 0.25M. The average error of the trials with 0.27M citrate (Nos. 1 to 11) is 0.00% with an average deviation of ±0.08%, and with 1.0M citrate the average error was −0.05 ± 0.07%. The average error of all the trials is −0.02% with an average deviation of ± 0.08%. The very small average error indicates the absence of any significant *systematic* fault, and the individual errors must be largely accidental. The known cumulative precision of the weighing, current measurement, and end-point detection, is much better than the observed average deviation. We believe that the average deviation is determined mainly by the time measurements. This is substantiated by the fact that the extreme errors (+0.31% and −0.22%) and the average deviation (± 0.08%) are very nearly the same as the observed extreme and average frequency variations of the power supply used to drive the clock. This variability can be eliminated by driving the clock from a power supply whose frequency is controlled more precisely than the utility power supply. Suitable frequency-controlled power supplies for this purpose are available commercially; *e.g.*, the Type 2005 unit manufactured by American Time Products, Inc., New York City.

If desired, the titration can be performed automatically with the instrument previously described[10].

With regard to practical application, any substance that is reducible by titanous ion is a potential interference. This includes a great many elements. Therefore, when maximal accuracy is desired it will be necessary to preliminarily separate the uranium from most other reducible elements. This same requirement is common to other methods used for precise uranium assays. It should be possible, however, to apply this titration in cases where the reduction potential of the accompanying element is sufficiently different from that of uranium (either greater or smaller) so that separate inflections are produced in the titration curve. The possibility of determining uranium in the presence of vanadium is of special significance, and is being investigated.

ACKNOWLEDGEMENT

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SUMMARY

In a citrate medium of pH 0.5 to 1.5 uranyl ion can be titrated to the $+4$ state with titanous ion generated by reduction of $+4$ titanium at a mercury cathode. By titrating at 85° equilibrium is quickly established, and the equivalence point is determinable with high precision by the usual potentiometric technique. The method is sufficiently accurate to serve for precise assays of macro amounts of uranium. Using a strictly constant generation current, and measuring time to the e.p., the average error of nineteen titrations of 28 to 112 mg quantities of uranium was −0.02%.

RÉSUMÉ

En solution tampon de citrate, de pH 0.5 à 1.5, l'ion uranyle peut être titré par réduction en uranium (IV) au moyen du titane (III); ce dernier est obtenu par réduction du titane (IV) à la cathode de mercure. En effectuant la titration à 85° l'équilibre est rapidement établi et le point d'équivalence peut être déterminé avec une grande précision par la technique potentiométrique habituelle. Cette méthode est suffisamment exacte pour servir au dosage de l'uranium. Les auteurs ont obtenu, pour 19 titrations de 28 à 112 mg d'uranium, une erreur moyenne de 0.02%.

ZUSAMMENFASSUNG

In einer Zitrat-Pufferlösung von pH 0.5-1.5, kann das Uranyl-Ion durch eine Reduktion zu Uranium (IV) mit Hilfe von Titan (III) titriert werden. Das letztere wird durch Reduktion von Titan (IV) an der Quecksilber-Kathode erhalten. Bei der Ausführung der Titration bei 85°, ist das Gleichgewicht rasch hergestellt und der Umschlagspunkt kann mit einer grossen Präzision mittels der gewöhnlichen potentiometrischen Technik bestimmt werden. Diese Methode ist genügend exakt für eine Makrobestimmung des Uraniums. Die Autoren haben für 19 Titrationen von 28-112 mg Uranium einen mittleren Fehler von 0.02% erhalten.

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ELECTROMETRIC TITRATIONS WITH TWO POLARIZED SECOND-ORDER ELECTRODES

by

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I. INTRODUCTION

In recent publications on electroanalysis a considerable amount of attention has been paid to polarization curves of platinum electrodes under various circumstances and their application to the description and elucidation of electrometric titration methods[1,2]. As a result of these investigations, new methods have been developed and many long-known methods have been reinvestigated and based theoretically. In this connection much attention was attracted by the "dead-stop" titration[3], which had been known since 1926[4] and also by the potentiometric titrations with polarized electrodes[5], discovered in 1925[6], which had never attained practical importance in analytical chemistry.

One of the conclusions of this research has been the realization that both methods are border-line cases of one general method which can be called electrometric titration at constant resistance; these special cases can be realized by properly choosing the applied voltage and the total electric resistance of the titration apparatus[7,8]. A second conclusion is expressed by the rule that these symmetrical electrometric titrations* give the best results if at the end-point one reversible redox-system is replaced by another[3d].

All these results have been based on the electrochemistry of platinum electrodes. Only in a few cases have researches been made into electrochemical phenomena in this type of titration with electrodes which are in chemical equilibrium with a component of the titration reaction[9]. It seems possible to extend the sphere of this method by using second-order electrodes[10]. As contrasted with platinum or other metal electrodes, these are reversible with respect to both components of the titration reaction. As will be demonstrated, in this way titrations are possible which cannot be performed in the same solutions with two platinum electrodes[11] and which are more difficult using silver electrodes[9]. In order to determine the best conditions for such a titration the behaviour of the silver/silver chloride electrode has been studied. In this communication directions for preparation and manipulation of useful electrodes are given.

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* We use the term "symmetrical electrometric titration" to distinguish them from the methods using a reference electrode and thus detecting the end-point with the help of an asymmetric electrode combination.

At the termination of this inquiry we found that also BRADBURY[12] proposed in 1953 the use of Ag/AgCl electrodes for "dead-stop" titrations. However, he gives no directions for the practical application of this method.

II. THE POLARIZATION OF THE SILVER/SILVER CHLORIDE ELECTRODE

In applying the second-order electrodes in symmetrical amperometric titrations it became evident that several irregularities may arise, leading to large titration errors and sometimes making the titration completely impossible. It is plausible to suppose that they are caused by deflections in the polarization of the electrodes. Further knowledge of the factors determining the polarization effects may perhaps supply some indications about the correct preparation and treatment of the electrodes. Those factors must appear in the mathematical formulation of the polarization curve or must be ruled out during its derivation.

FIANDA AND NAGEL[13] give a description of polarization phenomena at the Ag/AgCl electrode which has been chosen as a starting point for the following discussion. In the case of this electrode AgCl is implicated in the adjustment of the electrode potential, as it is in equilibrium with the metallic phase as well as the solution. The structure of the AgCl upper layer is of no importance for the equilibrium potential, but has a great influence on the kinetic behaviour of the electrode, especially on the polarization by an electric current. Two different electron transitions are possible, which is illustrated by the two potential-fixing equilibria

$$(1)\quad \mathrm{Ag} \rightleftarrows \mathrm{Ag}^+ + \mathrm{e}$$

$$(2)\quad \mathrm{Ag} + \mathrm{Cl}^- \rightleftarrows \mathrm{AgCl} + \mathrm{e}$$

Therefore equilibrium is possible between the metallic silver and Ag^+ as well as AgCl, *i.e.* with the solution and with the upper layer. In consequence the contributions of these reactions to the total electrolysis current will in a certain solution be determined by the structure of this layer.

As can easily be shown, at high $[\mathrm{Ag}^+]$ and low $[\mathrm{Cl}^-]$ the electrode potential E is determined in the main by the first equilibrium: the electrode behaves as a simple silver electrode. On the other hand at high $[\mathrm{Cl}^-]$ only equilibrium (2) will determine the electrode potential.

In the electrochemical equilibria these simple electrodes follow the relation of Nernst:

$$(1)\quad {}_0E_1 = {}_0e_1 + \frac{RT}{F}\ln\,[\mathrm{Ag}^+]\quad ({}_0e_1 = 0.800\ \mathrm{V})$$

$$(2)\quad {}_0E_2 = {}_0e_2 - \frac{RT}{F}\ln\,[\mathrm{Cl}^-]\quad ({}_0e_2 = 0.220\ \mathrm{V})$$

In general, both ions are present in solution and ${}_0E_1 = {}_0E_2 = {}_0E$. If the equilibrium at this electrode is disturbed ${}_0E_1$ and ${}_0E_2$ will deviate from ${}_0E$. This will be the case, for instance, when Cl^- or Ag^+ is added to the solution.

We call $\triangle E_1 = {}_0E - {}_0E_1$ the overpotential of the forward reaction 1
$\triangle E_2 = {}_0E - {}_0E_2$ the overpotential of the forward reaction 2
Both reactions will proceed to reach again an equilibrium $\triangle E_1 = \triangle E_2 = 0$.

An electric current i, passing the electrode, also disturbs the equilibrium, causing a polarization effect by changing ${}_0E$ into ${}_iE$. In this case the overpotentials of the electrode reaction are called polarization overpotential ${}_i(\triangle E_1)$ or ${}_i(\triangle E_2)$.

If both reactions are proceeding in a forward direction (anode reaction), ${}_i(\triangle E)$ is taken to be positive. At the same time at the cathode the reversed reaction takes place and there ${}_i(\triangle E) < 0$. These polarization overpotentials can be caused by different mechanisms, mostly based on retarding of the electrode reactions by an electric resistance at the electrode surface or a reduction of the ion mobilities in a thick surface layer. Thirdly the velocities of the electrode reactions can be determined directly by the concentration gradient in the electrode-solution interface so that the free ion diffusion regulates the polarization effects of an electric current. Moreover, chemical changes in the surface layer can take place as a result of electric current, also causing deviations of the electrode potential.

As the velocities of the reactions 1 and 2 can be ruled by various mechanisms, the nature of the resulting polarization effect will in general depend on several factors, given by the structure of the electrode and the composition of the solution.

In the simplest case the electrical and mechanical resistances in the surface layer are very low and the electrode itself is not changed by the current. Then the velocities of both electrode reactions are ruled by the same mechanism, the diffusion velocities of the related ions.

As there is a direct relation between diffusion velocity and ion concentrations, this simplest second-order electrode promises well for the determination of ion concentrations.

In this case of a concentration polarization the total polarization current can be described as the sum of the currents accompanied by the two separate electrode reactions[13].

As the polarization overpotential is exclusively determined by the concentration gradient in the diffusion layer, this borderline case of the silver electrode can be written:

$$_i(\triangle E_1) = {}_iE - {}_\circ E_1 = {}_\circ e_1 + \frac{RT}{F} \ln [Ag^+]_\circ - {}_\circ e_1 - \frac{RT}{F} \ln [Ag^+] = \frac{RT}{F} \ln \frac{[Ag^+]_\circ}{[Ag^+]},$$

where $[Ag^+]_\circ$ = concentration of Ag^+ in the electrode - diffusion layer interface

$[Ag^+]$ = concentration of Ag^+ in the bulk of the solution.

In the same way $_i(\triangle E_2) = \frac{RT}{F} \ln \frac{[Cl^-]}{[Cl^-]_\circ}$

The partial current i_1 can be calculated by considering[14] that the number of g-ions passing a diffusion layer per unit of time is equal to $M = [M] . O.U.K.$,

where $[M]$ = ionic concentration in g-eq./l

O = effective surface of the diffusion layer

U = ionic velocity at a potential gradient of 1 V/cm

K = the force acting on the ions.

If the diffusion potential can be ignored, the acting force is proportional to the flux of the thermodynamic potential in the diffusion layer, so

$$K = RT \frac{\delta \ln [M]}{\delta x}$$

$$\text{As } M \cdot \frac{\delta \ln [M]}{\delta x} = \frac{\delta [M]}{\delta x},$$

$$M = O.U.RT \frac{\delta [M]}{\delta x}$$

In a thin diffusion layer with $\triangle x = d$ applies the equation

$$M = \frac{R.T.O.U. ([M]_\circ - [M])}{d}$$

As every g-eq. transports F Coulombs and as 1 A = 1 Coulomb/sec,

$$i = F.M, \text{ so } i_1 = \frac{R.T.O.l_{Ag^+} ([Ag^+]_\circ - [Ag^+])}{d}$$

where l_{Ag^+} = equivalent ionic conductance $= \frac{U.F}{P}$

and P = electric potential gradient, in defining U fixed at 1 V/cm.

In the same way it is found that $i_2 = - \frac{R.T.O.l_{Cl^-} ([Cl^-]_\circ - [Cl^-])}{d}$

It has been shown that $_i(\triangle E_1) = \frac{RT}{F} \ln \frac{[Ag^+]_\circ}{[Ag^+]}$ and $_i(\triangle E_2) = - \frac{RT}{F} \ln \frac{[Cl^-]_\circ}{[Cl^-]}$.

As in presence of solid AgCl $[Ag^+]_\circ \cdot [Cl^-]_\circ = [Ag^+] \cdot [Cl^-] = L_{AgCl}$.

$\ln \frac{[Ag^+]_\circ}{[Ag^+]} = - \ln \frac{[Cl^-]_\circ}{[Cl^-]}$, therefore $_i(\triangle E_1) = {}_i(\triangle E_2) = {}_i(\triangle E)$

Thus $[Ag^+]_\circ = [Ag^+]\, e^{\frac{_i(\triangle E).F}{RT}}$ and $[Cl^-]_\circ = [Cl^-]\, e^{-\frac{_i(\triangle E).F}{RT}}$

Substitution in the relations for i_1 and i_2 results in the expression i as a function of the polarization potential $_iE$.

The theoretical treatment of the most promising Ag/AgCl electrode gives the following equation of the polarization curve:

$$i = \frac{R.T.O}{d}\, l_{\mathrm{Cl}^-} \frac{L_{\mathrm{AgCl}}}{[\mathrm{Ag}^+]} \left(1 - e^{-\frac{F}{RT}\left({}_iE - {}_oe_1 - \frac{RT}{F} \ln [\mathrm{Ag}^+]\right)}\right) + \\ - \frac{R.T.O}{d}\, l_{\mathrm{Ag}^+} [\mathrm{Ag}^+] \left(1 - e^{\frac{F}{RT}\left({}_iE - {}_oe_1 - \frac{RT}{F} \ln ([\mathrm{Ag}^+])\right)}\right)$$

This implies that an equation $i = f\,({}_iE, [\mathrm{Ag}^+])$ is valid if there is no retardation of the electrode reaction by resistances at the electron or ion transfer nor any structural change in the electrode surface, so that the polarization phenomenon exclusively is determined by the velocity of the ion diffusion.

From this theory in combination with several experimental results we draw some conclusions concerning the subject of our investigation:

(a) In applying a potential difference V between two similar electrodes, E of both electrodes will change according to

$$\frac{(\mathrm{d}E)_{\mathrm{cathode}}}{\mathrm{d}V} < 0 \quad \text{and} \quad \frac{(\mathrm{d}E)_{\mathrm{anode}}}{\mathrm{d}V} > 0$$

so that voltage V results in a polarization tension between the electrodes equal to $\triangle_i E = ({}_iE)_{\mathrm{anode}} - ({}_iE)_{\mathrm{cathode}}$, caused by the polarization current

$$i = \frac{V - \triangle_i E}{R + r}, \text{ in which}$$

R = external resistance of the apparatus
r = internal resistance of the electrolysis cell
If both electrodes satisfy the conditions under which
$i = f\,({}_iE, [\mathrm{Ag}^+])$, then in electrolysis the equation
$i = F\,(\triangle_i E, [\mathrm{Ag}^+])$ is applicable.
Hence, at constant i : $(\triangle_i E)_i = F'\,([\mathrm{Ag}^+])$
at constant $\triangle_i E$: $(i)_{\triangle_i E} = F''\,([\mathrm{Ag}^+])$

Therefore the course of a titration can be followed by measuring $\triangle_i E$ or i, to the effect that a potentiometric or amperometric titration is performed with the aid of two similar polarized second-order electrodes. This is possible on condition that the titration curves indicate sharply the point $[\mathrm{Ag}^+] = [\mathrm{Cl}^-]$. The theoretical titration curves, derived from calculated polarization curves fulfil this stipulation. So the circumstances supposed in the construction of these titration curves have to be realized experimentally.

(b) During a titration $\triangle_i E$ or i should be as constant as possible.

(c) The electric resistance in the titration apparatus and in the electrolysis cell should be low. This can be ensured by adding an indifferent electrolyte to the solution. We always add 5 ml saturated solution of $\mathrm{Mg(NO_3)_2}$ to 30 ml sample solution.

(d) Chemical or mechanical alterations of the electrode surface during a titration are not allowed, so the preparation of the silver surface and the silver chloride layer requires special attention.

(e) In order to prevent alterations of the electrodes by the electric current, intensive or too long polarization should be avoided. For this purpose titrations are performed as quickly as possible and at a low electrolysis voltage; after each determination the electrodes are electrically interchanged by means of a commutator.

(f) The value of $\frac{R.T.O}{d}$ has to be a constant during a titration.

Therefore the temperature should not vary, the effective surface should not alter (for instance, by release of silver chloride particles) and the diffusion layer should have a constant, low thickness as i decreases sharply at rising value of d. The last requirement appears to be very important. The manner and the velocity of stirring are of the greatest importance, and it is always necessary that the standard solution reacts completely before reaching the electrodes. This can be ensured by a suitable insertion of the burette tip in the titration vessel.

(g) The mobility of the ions (expressed in the equivalent ionic conductance l) should be constant and as high as possible. This can be attained by a thin and very porous AgCl surface layer. A thick layer with relatively few and small pores, obtained by electrolytic precipitation of chlorine on silver at high current density or over a long period, results in irregular titrations and in the impossibility of determinations with much diluted standard solutions, as equilibrium is reached very slowly after every addition.

In fact polarization phenomena appear in this case, which are excluded in the above-mentioned expression of the polarization curve. On the other hand, the silver chloride layer should not be too thin or it will dissolve in a short time and give bad results. The correct compromise between a thin layer and a sufficiently big mass of AgCl is promoted by making the electrode surface as large as possible.

(h) By comparing the polarization curves found by means of these electrodes with the calculated curves, we can check the quality of the electrodes with regard to the above-mentioned requirements.

These eight conclusions served as a guide in the investigations on the most suitable conditions for determination of chloride using Ag/AgCl electrodes and will be referred to in the description of the electrodes and the titration apparatus

III. PREPARATION OF THE SILVER ELECTRODE.

It will be necessary to precipitate the AgCl layer on a clean and regular silver surface (II, d). The disadvantage of solid silver electrodes is a very fast wastage through the repeated precipitation and removal of AgCl. For this reason we use silver-plated platinum wire in order to obtain a smooth and large (II, g) surface and because disk, gauze, or tube-shaped electrodes produce difficulties in effective stirring (II, f).

In a critical review JANZ AND TANIGUCHI[15] deal with the silver/silver chloride electrode and arrive at the conclusion, that the electrolytic preparation of a well-reproducible electrode has to meet the following requirements:

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1. Before being plated, the platinum electrode should be treated with concentrated nitric acid and thoroughly washed with distilled water.
2. The silver plating solution must not contain free cyanide ions. This solution is prepared by dissolving solid AgCN in a hot, filtrated 20% solution of KCN in water and stirring intensively for half an hour. The excess AgCN is filtered off and after cooling solid $KAg(CN)_2$ crystallizes. It is recrystallized twice in distilled water and dried at room temperature. We use a 1% solution of this salt in boiled distilled water after having precipitated any small amounts of free cyanide by adding very dilute $AgNO_3$ (*ca.* 0.005*N*) till a faint turbidity becomes visible.
3. The cathode compartment should be separated from the anode in order to prevent defilement with anodic electrolysis products. Here we use a NH_4NO_3-agar bridge.
4. Silver plating goes on for 4.5 hours at a current density of about 1.7 mA/cm² with intensive stirring.
5. The silver-plated electrodes should be immersed in concentrated ammonia for a few seconds and, immediately after that, washed with distilled water for 8 hours. We confine ourselves to washing with 60 l distilled water running through a small vessel which contains the electrodes.

Electrode prepared in this way have a dull, velvet-like, silvery-white appearance and can be stored in distilled water.

IV. PREPARATION OF THE SILVER/SILVER CHLORIDE ELECTRODE

JANZ AND TANIGUCHI (*loc.cit.*) give no directions for the preparation of a silver chloride layer suitable for our purpose (II, d, g) as they deal only with reference electrodes for currentless measurements.

FIANDA AND NAGEL (*loc.cit.*) recommend alternating anodic and cathodic polarization of the electrode in a solution of KCl and KNO_3, followed by anodic loading for a short time. In this way they obtain polarization curves in rather good conformity with the theoretical ones. However, the authors give no exact description of their recipe. A number of experiments on this subject produced the following instructions:

The silver-plated electrodes are polarized positively for 10 sec. in a 2% solution of KCl containing 0.1% KNO_3, at a current density of 2.0 mA/cm². A platinum wire is used as cathode. Then the potential difference is reversed by means of a commutator and the silver electrode functions as a cathode for 5 sec. This procedure is repeated ten times, followed by chlorinating the silver electrode for 10 min at 2.25 mA/cm². The solution is not stirred.

The electrodes should have a regular, dark-brown appearance. They may be stored in distilled water in the dark; titration in dark vessels is not necessary.

V. THE TITRATION APPARATUS

The voltage, regulated by potentiometers P_1 and P_2 (Fig. 1) is applied to the electrodes C_1 and C_2 by way of commutator S_1 (II, e, also used in part IV) and is measured by the millivoltmeter V (Multavi I, Hartmann & Braun, Frankfurt/Main). The polarization current *i* can be varied by means of resistor R and is measured by a sensitive galvanometer (Radiometer Type GVM 22a, Copenhagen). The narrow point of an ammonium nitrate-agar bridge B is fitted just between the two electrodes and is connected with a saturated calomel electrode K by way of a 80% solution of NH_4NO_3 in water. The potential difference E ($_iE$ or $_0E$) between K and C_1 or C_2 is measured currentless by a vacuum-tube voltmeter (pH-meter Electrofact, Amsterdam).

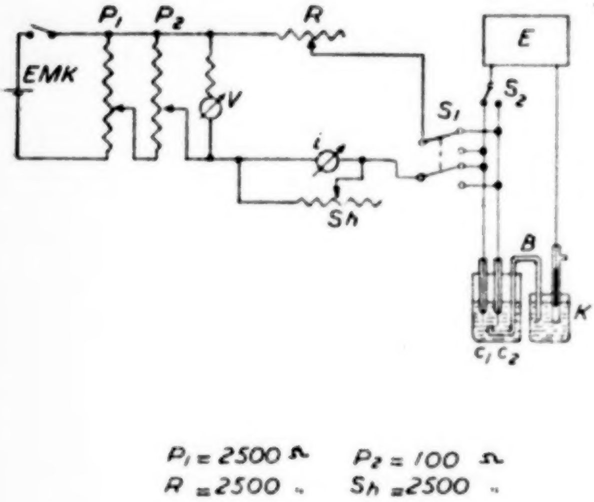

Fig. 1. Circuit for titration and determination of polarization curves.

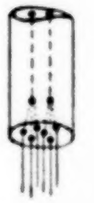

Fig. 2. Schematic representation of large surface electrode.

The electrodes are constructed as follows:

Two platinum wires, each 2 cm long with 2 mm diameter are soldered to copper wire which will be covered by glass-fabric isolation tube and embedded in polythene. This is done by means of a little bar of burning polythene, the melted plastic being dropped on to the isolation material. The isolated copper wires are fused together and enveloped in polythene. Then the platinum electrodes are silver-plated and chlorinated. This electrode assembly is unbreakable, does not occupy much room and makes impossible any change in the mutual position of the two electrodes.

An electrode combination with a large surface(II, g) is easily constructed by connecting several platinum wires to one electrode (Fig. 2). We use a specimen with six wires and a total surface of 4.5 cm².

It has been shown that a rotating titration vessel is necessary. FIANDA AND NAGEL (*loc. cit.*) also use one. It should be placed on a synchronous electromotor, because all other motors cause great deflections in the value of *i*, probably in consequence of variations in the diffusion layer by variable stirring velocity(II, f). We use a bicycle-dynamo, connected by way of a transformer with the electric-light mains (50 Hz. AC.) as a cheap motor.

In order to prevent the solution from being swung out of the rapidly rotating vessel, a resting polythene stirrer is attached to the electrode assembly. It may also be fixed to a glass tube which serves as supply-pipe for nitrogen in titrations which are inter-

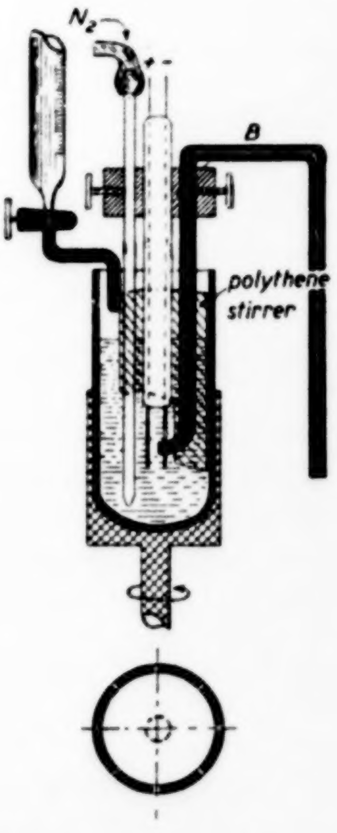

Fig. 3. Titration cell with agar bridge.

fered with by oxygen. Fig. 3 shows this titration-cell. The bakelite electrode-holder is attached to a support and can be shifted vertically to make possible rapid interchange of titration vessels. This figure also gives a horizontal section of the titration vessel holder, made of one piece of copper.

VI. RESULTS

In Fig. 4 some polarization curves are plotted, which are determined by means of the described electrode with several silver ion concentrations. The measured potentials have been converted into electrode potentials by fixing the saturated calomel electrode at 250 mV. Then the anode potential is plotted against the measured value of *i*, the cathode potential against -*i*. In such a diagram, *i* can be found for every value of $\triangle_i E$ by putting it on the horizontal axis in such a way that the corresponding $i_{\text{anode}} = -i_{\text{cathode}} = i$. The steeper this polarization curve passes its point $i = 0$, the higher will be $\frac{i}{\triangle_i E}$ and the lower $\frac{\triangle_i E}{i}$ in this region. Consequently, the higher will be the current in an amperometric titration and the lower the measured voltage in potentiometric titration. Fig. 4 shows a distinct correlation between this shape and the silver ion concentration.

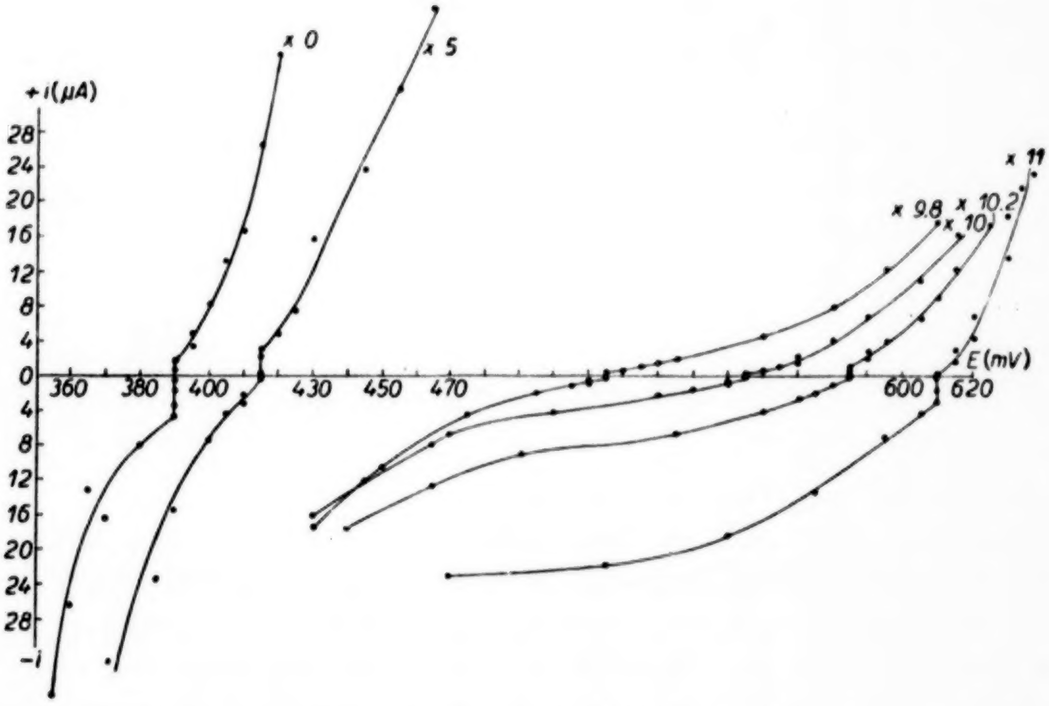

Fig. 4. Polarization curves during titration of chloride with silver nitrate.
Solution: 10 ml 0.02*N* NaCl; 20 ml H_2O; 5 ml $Mg(NO_3)_2$ conc.; *x* ml 0.02*N* $AgNO_3$.

To check these curves(II, h), we calculated a number of theoretical polarization curves. To this end the polarization equation is modified to

$$\frac{i}{A} = \frac{L_{\text{AgCl}}}{[\text{Ag}^+]}\left(1 - e^{-\frac{F}{RT}\left({}_iE - {}_0e_1 - \frac{RT}{F}\ln[\text{Ag}^+]\right)}\right) + $$
$$-[\text{Ag}^+]\left(1 - e^{\frac{F}{RT}\left({}_iE - {}_0e_1 - \frac{RT}{F}\ln[\text{Ag}^+]\right)}\right)$$

where $A = \frac{R.T.O}{d} l_{Cl^-}$ or $\frac{R.T.O}{d} l_{Ag^+}$ and $l_{Cl^-} \approx l_{Ag^+}$

F = 96500 Coulomb
R = 8,315 Joule
T = 290 °K
$L_{AgCl} = 1 \times 10^{-10}$.

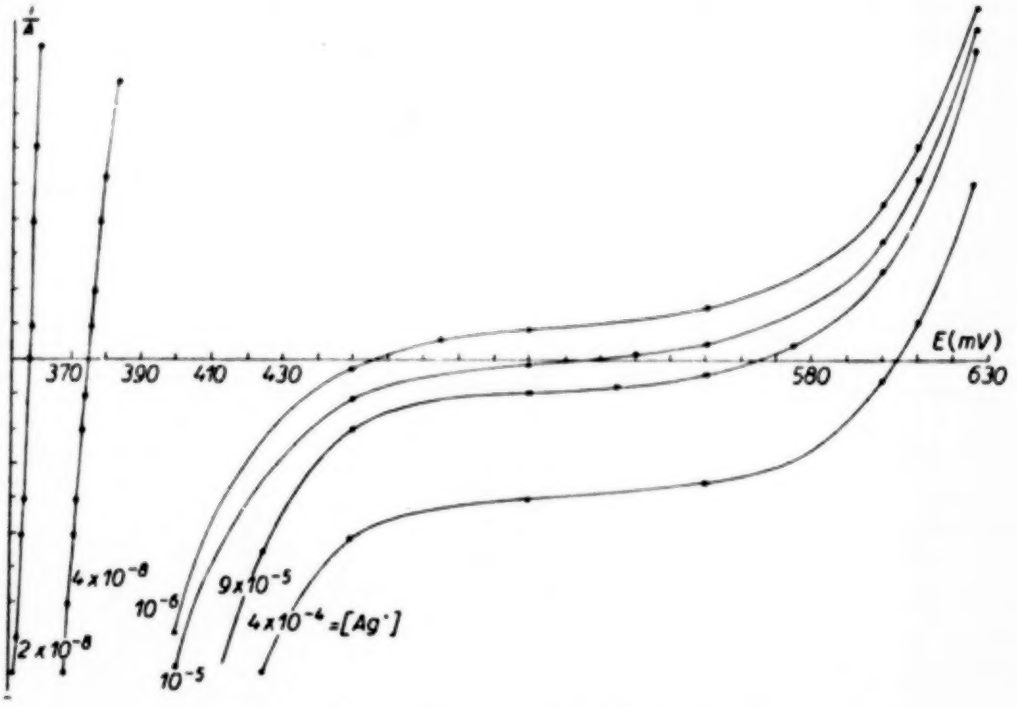

Fig. 5. Theoretical polarization curves.

Fig. 5. shows the result of these calculations. There is a good conformity with the experimental curves: at the beginning of the titration $\frac{di}{dE}$ decreases with increasing $[Ag^+]$ and then increases after the equivalence point ($[Ag^+] = 10^{-5}$) has been reached. This effect is demonstrated clearly with the curves $(\triangle_i E)_i = F'([Ag^+])$ and $(i)_{\triangle_i E} = F''([Ag^+])$ (Fig. 6): in the end-point of the titration $(i)_{\triangle_i E}$ is minimal whilst $(\triangle_i E)_i$ has its maximum value (II, a).

As appears from $(i)_{\triangle_i E = 30\ \mathrm{mV}} = F''([Ag^+])$ in Fig. 7, Fig. 4 results in a similar titration curve. This is compared with some experimental titration curves, found by means of different electrodes in different solutions. We always found a definite miminum in the equivalence point, as may be expected from the reasonable conformity between theoretical and experimental polarization curves. The practical titration curves are different in position with respect to the current-axis. This is brought about by differences in electrical resistance, because $i = \frac{V - \triangle_i E}{R + r}$. We notice considerably sharper end-points at higher currents and thus at lower resistances.

Therefore the electrodes conform quite closely the requirements of the — for our purpose — most plausible theory of the Ag/AgCl electrode.

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Small deviations in the polarization curves are probably caused by the fact that the polarization phenomena are not exclusively determined by ion diffusion in all cases; the theoretical circumstances cannot be realized completely. However, this is of no importance for the titration.

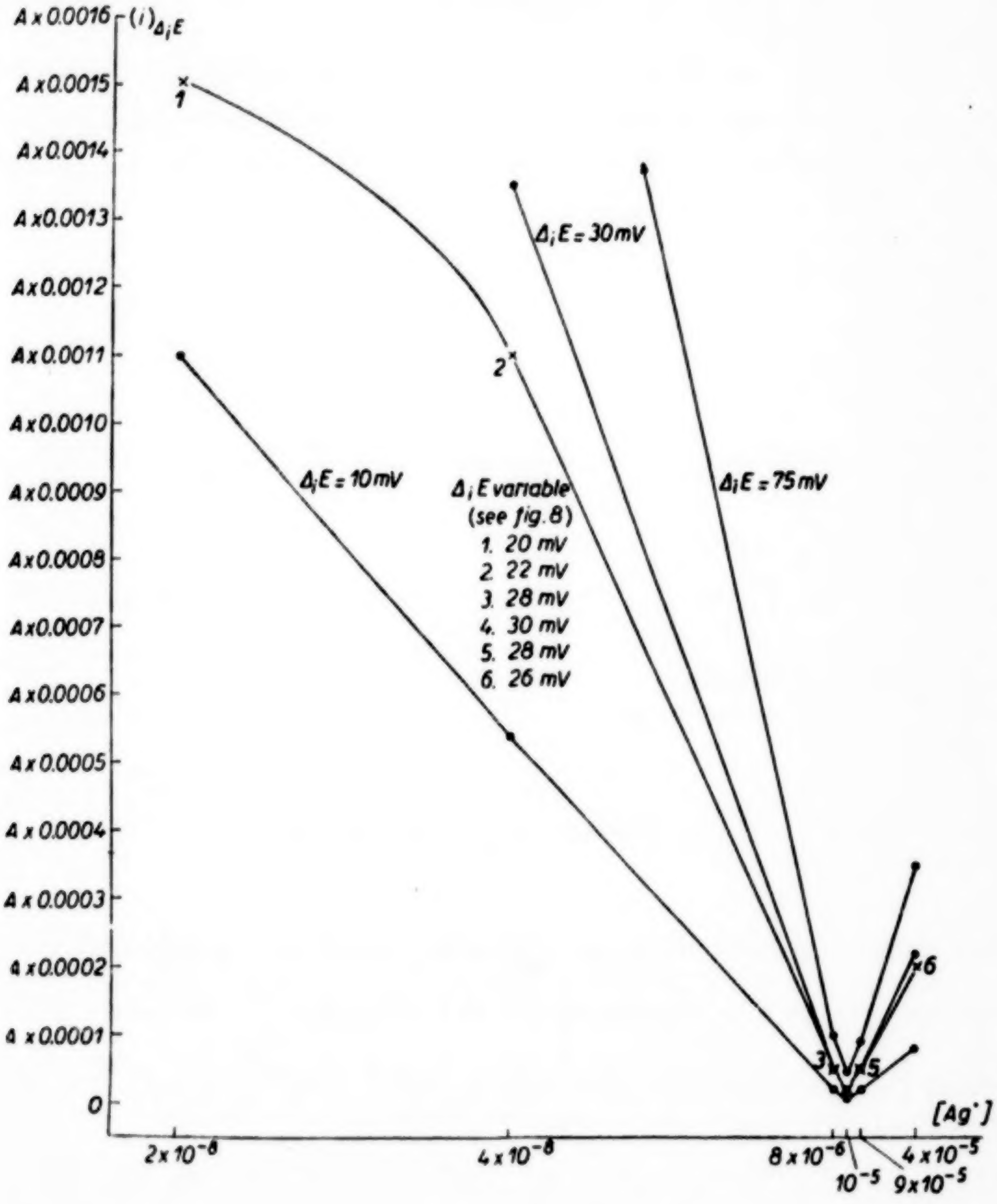


Fig. 6. Theoretical amperometric titration curves, derived from Fig. 5.

In the derivation of an amperometric titration curve $\triangle_i E$ is assumed to have a constant value(II, b). This is more practicable in proportion as in $i = \dfrac{V - \triangle_i E}{R + r}$ the value of $R + r$ is nearer to 0: then also $V - \triangle_i E$ must become 0, so $\triangle_i E$ gets the constant value V.

In reality $R + r$ always has a certain value; nevertheless good results can be attained, as is shown clearly in Fig. 7, for different resistance values. In Fig. 6 a theoretical titration curve with variable $\triangle_i E$ is presented. Indeed $\triangle_i E$ is not constant as is demonstrated in Fig. 8. In the end-point $R + r = \dfrac{V - \triangle_i E}{i} = \dfrac{30 - 28}{0.0085} = 235.5\ \Omega$. Here $\triangle_i E$ reaches a maximum value and

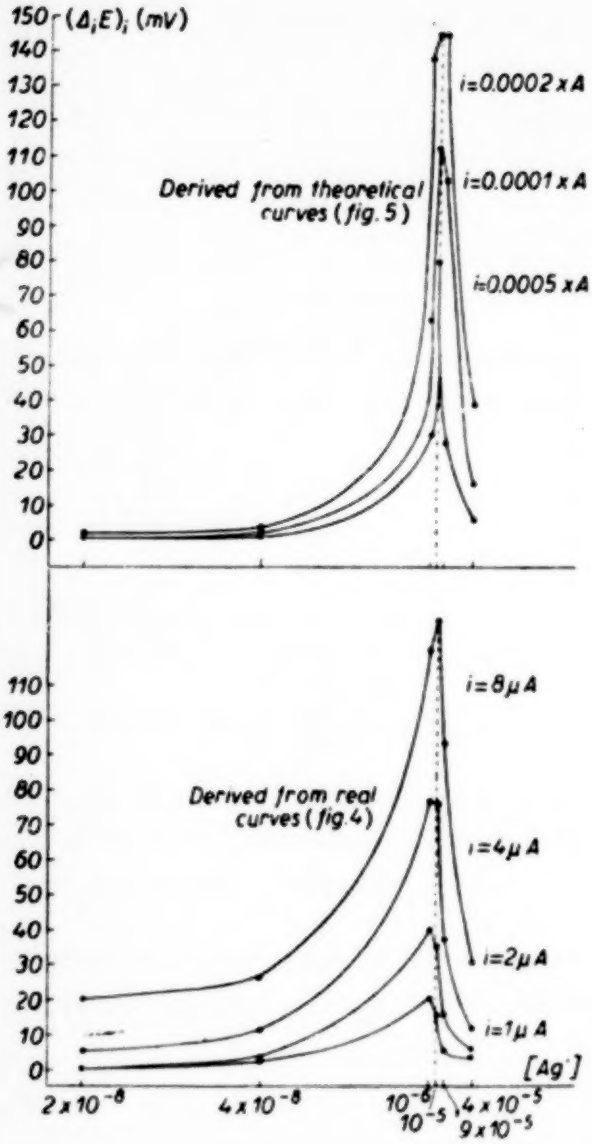
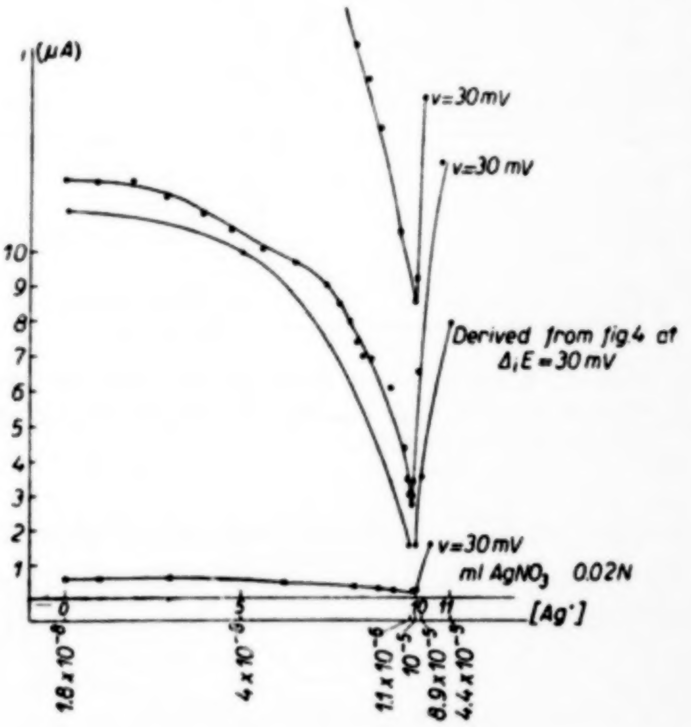


Fig. 6a. Theoretical potentiometric curves, derived from Fig. 5 compared with derivation from Fig. 4.

Fig. 7. Experimental amperometric titration curves compared with titration curve as derived from Fig. 4.



thus can also indicate the end-point. This will be the more obvious as i becomes more constant with increasing values of V and $R + r$. In this way the border-line case of the symmetric potentiometric titration with second-order electrodes is approached (Fig. 6a). Several experiments showed that the amperometric titration is to be preferred, because the differences between the slopes of the real polarization curves at the end-point are rather small and irregular in the region of the low current values used in this potentiometric method.

VII. APPLICATIONS

The best titration results are obtained by adding the standard solution rather quickly and regularly. In titrations with solutions no more dilute than 0.005N, i decreases remarkably quickly just previous to the end-point so that the latter can be found within a few drops. The optimum value of V is situated between 10 and 80 mV. If the electrodes are easily changed by the current, as can be seen after setting V to 0 mV, titration at V = 10 mV and taking a higher voltage just before the end-point will give good results.

The galvanometer light-spot should follow the titration very quickly and must not be allowed to oscillate. Otherwise stirring will be insufficient or the standard solution will be added too close to the electrodes. The method is especially useful for titrations

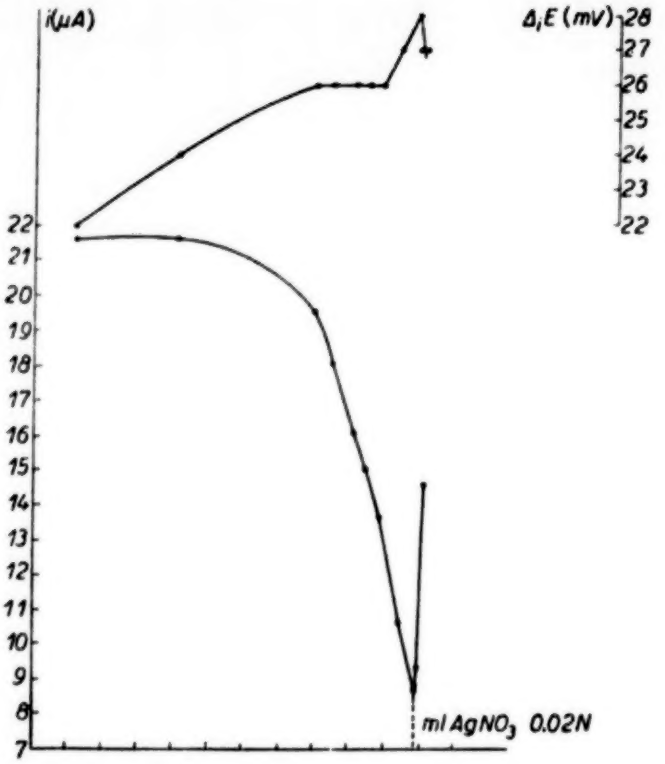


Fig. 8. Amperometric and simultaneous potentiometric titration curve of 10 ml HCl, *ca.* 0.02N. V = 30 mV.

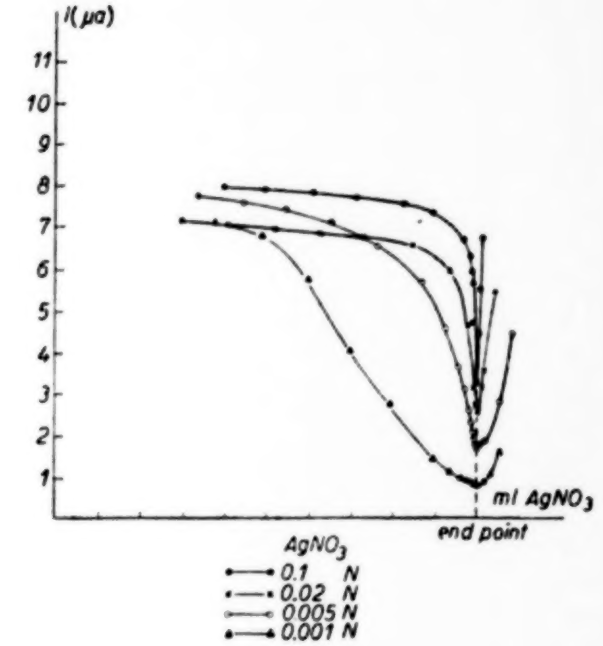


Fig. 9. Amperometric curves for titrations with different dilution. V = 75 mV.

with very dilute solutions and in colloidal or dirty samples containing little chloride[10]. By means of Ag/AgI - and Ag/AgBr-electrodes prepared in the same manner, titrations of iodides and bromides can be performed.

(1) *Titrations with diluted solutions*

In Fig. 9 curves are shown of titrations with 0.1N, 0.02N, 0.005N and 0.001N solution of $AgNO_3$. In the last case the titration is also possible without graphical determination of the end-point. Then the maximum titration error amounts to 0.2 ml solution, corresponding with $0{\cdot}2 \times 0.001 = 2{\cdot}10^{-4}$ meq. on 45 ml or $4.5{\cdot}10^{-6}$ meq./ml, independent of the starting volume. This result was obtained by means of the electrodes represented in Fig. 2. As electrometric titrations are easily performed in rather small volumes, titrations of very small quantities of chloride are possible.

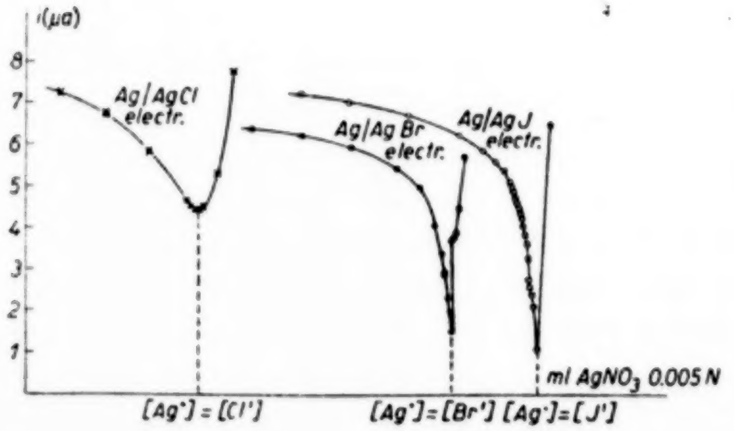


Fig. 10. Amperometric curves for titration of chloride, bromide and iodide with 0.005N $AgNO_3$. V = 30 mV.

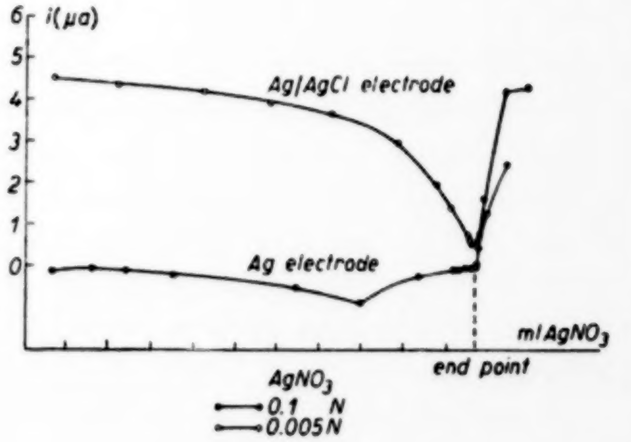


Fig. 11. Effect of AgCl surface layer.

(2) Titration of iodides and bromides

Fig. 10 shows Br^--and I^--titrations curves as compared with the Cl^--curve, for titrations with 0.005N $AgNO_3$ at the same electrodes, covered with Ag/AgBr, Ag/AgI and Ag/AgCl respectively.

VIII. DISCUSSION

Several methods for electrometric titration of halides are now available. Tabulated below are those most generally used.

Electrodes	*Indication of the end-point*	*Reference*
Unpolarized		
Ag—calomel	$d\triangle\,{}_0E/dx$ maximum	16
Ag—quinhydrone (${}_0E = E_{eq}$)	$\triangle\,{}_0E = 0$ ($i = \dfrac{\triangle\,{}_0E}{R + r} = 0$)	17
Ag—Ag/$AgNO_3$ (${}_0E = E_{eq}$)	ditto	18
Ag—Ag/$AgNO_3$ 0.01N	$d\triangle\,{}_0E/dx$ maximum	19
Ag—Ag/Ag-ion exchange resin	ditto	20
Polarized		
Rotating Pt — calomel	Increase of i_{diff}	21
Ag—Ag	Increase of i	9a
Pt—Pt with nitrite	Increase of i	11
Ag—Ag	Obtuse minimum of i at slow titration	9b
Ag/AgCl—Ag/AgCl	Sharp minimum of i at quick titration	10

As contrasted with the other methods the one discussed in this communication gives a very sharp end-point in a quick titration with dilute standard solutions independently of the sample composition and the stability of a reference electrode. The benefit of the AgCl-layer is evident in Fig. 11, where a titration with 0.1N $AgNO_3$ by means of Ag electrodes is compared with a titration at Ag/AgCl electrodes by 0.005N $AgNO_3$.

This result agrees with SALOMON's experiments (9a). MASTEN AND STONE (9b) record an obtuse minimum using silver electrodes. We have not been able to find such a curve reproducible in titrations with solutions more dilute than 0.1N.

The author is indebted to Miss G. A. ROEDE for her preparation of many electrodes and the skilful way in which she performed the large number of determinations necessary for this investigation.

SUMMARY

Electrometric titrations at constant resistance with two polarized second-order electrodes are shown to be possible. The polarization curve of the silver/silver chloride electrode is investigated theoretically and experimentally in order to find the best conditions for chloride titrations.

Directions are given for the preparation and manipulation of electrodes which enable quick titrations with rather dilute standard solutions (up to 0.001N $AgNO_3$). The titration apparatus used and some practical applications of the amperometric titration are described.

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RÉSUMÉ

La possibilité de dosages électrométriques à résistance constante, à l'aide de deux électrodes de second ordre, polarisées, est démontrée.

Pour trouver les conditions les plus aptes au titrage des chlorures, la courbe de polarisation de l'électrode argent/chlorure d'argent est examinée. Les directives pour la préparation et l'application des électrodes obtenues de cette façon permettent des titrages rapides avec des solutions étalon passablement diluées (jusqu'à 0.001 N $AgNO_3$).

Le dispositif utilisé et quelques applications pratiques du dosage ampérométrique sont décrits.

ZUSAMMENFASSUNG

Die Möglichkeit elektrometrischer Massanalysen bei konstantem Widerstand mittels zweier polarisierter zweifacher Elektroden wird angezeigt.

Um die besten Verhältnisse für Chloridtitrationen zu ermitteln, wird die Polarisations-Strom Kurve der Silber/Silberchloridelektrode theoretisch und experimentell untersucht. Hierbei ergeben sich Anweisungen für die Bereitung und Anwendung von Elektroden, welche schnelle Titrationen mit ziemlich verdünnten Lösungen (bis zu 0.001 N $AgNO_3$) ermöglichen.

Der gebrauchte Titrationsapparat und einige praktische Anwendungen der amperometrischen Bestimmungsweise werden beschrieben.

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A HIGH-FREQUENCY TITRATION APPARATUS

by

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INTRODUCTION

Extensive use of high-frequency titrimeters has been restricted by the high cost, complex circuitry and difficulty of construction and modification of present instruments. To overcome these obstacles an easily-constructed inexpensive high-frequency titration apparatus was proposed by HALL[6].

An instrument similar to that of HALL was built but after using it for a number of preliminary titrations, several limitations became evident. The most serious of these was the fact that when no series capacitor was used with the titration cell, oscillation was often completely damped out by the conductance of the solution under test. This possibility was mentioned by HALL. When the switch selecting the series capacitor was set so that the oscillator could be made to fall into oscillation throughout the titration, the instrument was relatively insensitive. Moreover, if any of the series capacitors were used, each of the two leads to the titration cell was sensitive to capacitance changes between it and the ground (chassis), making effective shielding of the cable from the instrument to the titration cell impossible.

A final disadvantage was the fact that the method employed by HALL to determine changes in effective capacity, described in detail by BENDER[1], requires that the capacitance of the variable condenser be decreased slowly until the circuit falls into oscillation, causing a rise in negative grid bias, indicated by a closing of the electron-ray tube. At this point, turning of the variable capacitor knob must be stopped. If the capacitor has been turned past the point where oscillation begins, it is not possible to turn back (increase the capacity) to that point to get the reading, since the circuit falls into oscillation nearer the resonant frequency than it falls out of oscillation.

In order to overcome these limitations, the present apparatus was designed and constructed from readily available parts. A number of features of HALL's apparatus were incorporated in the circuit of this instrument. This titrimeter, used frequently in our laboratory for over two years, has been found to be satisfactory and reliable. Recently HALL *et al.*[8], published a modification of his original apparatus employing separate tubes for oscillator and oscillation indicator.

APPARATUS

The instrument has been designed to respond to either effective capacitance or effective resistance changes in the titration cell circuit. The schematic diagram of the apparatus is given in Fig. 1 and a photograph of the complete titration assembly is shown in Fig. 2. The circuit employs a type 6V6 (metal) tube as a crystal oscillator. The titration cell is coupled to the tank circuit of the oscillator by means of a coaxial cable and radio-frequency connectors. A type 6E5 electron-ray tube serves to indicate the grid bias of the oscillator tube. A type 6X5GT/G tube is used as a full-wave rectifier to supply the B voltage for the tubes. A switch is provided which allows the use of either this B supply or an external supply.

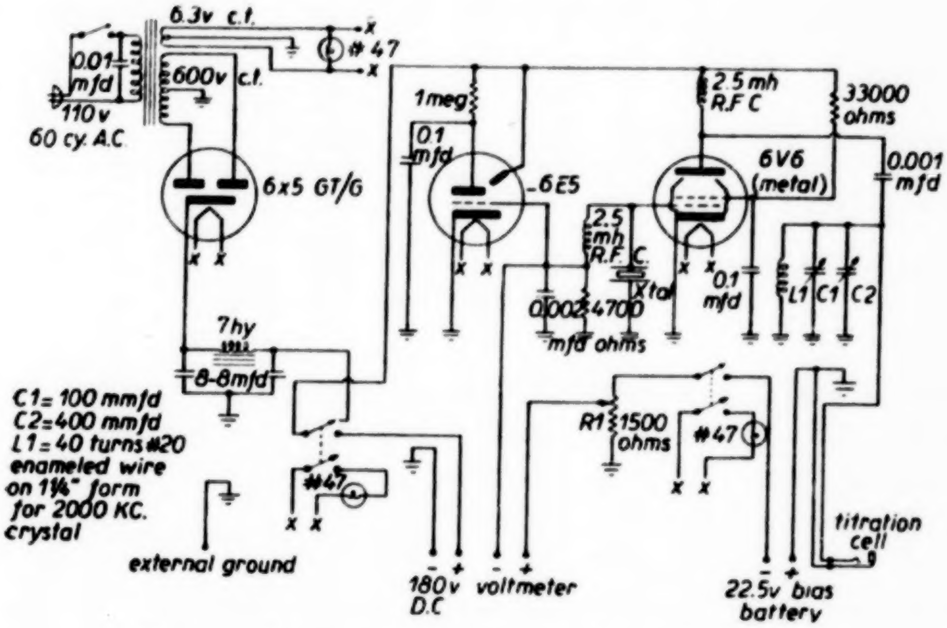
6.3v c.t.
#47
0.01 mfd
600v c.t.
110 v
60 cy. A.C.
6x5 GT/G
1meg
0.1 mfd
6E5
2.5 mh R.F.C
33000 ohms
6V6 (metal)
0.001 mfd
2.5 mh R.F.C.
Xtal
0.002 mfd
4700 ohms
0.1 mfd
L1
C1
C2
7hy
8-8mfd
C1= 100 mmfd
C2=400 mmfd
L1= 40 turns #20
enameled wire
on 1¼" form
for 2000 KC.
crystal
#47
R1 1500 ohms
#47
x
external ground
180v D.C
voltmeter
22.5v bias battery
titration cell
- +

Fig. 1. Schematic diagram of the apparatus.

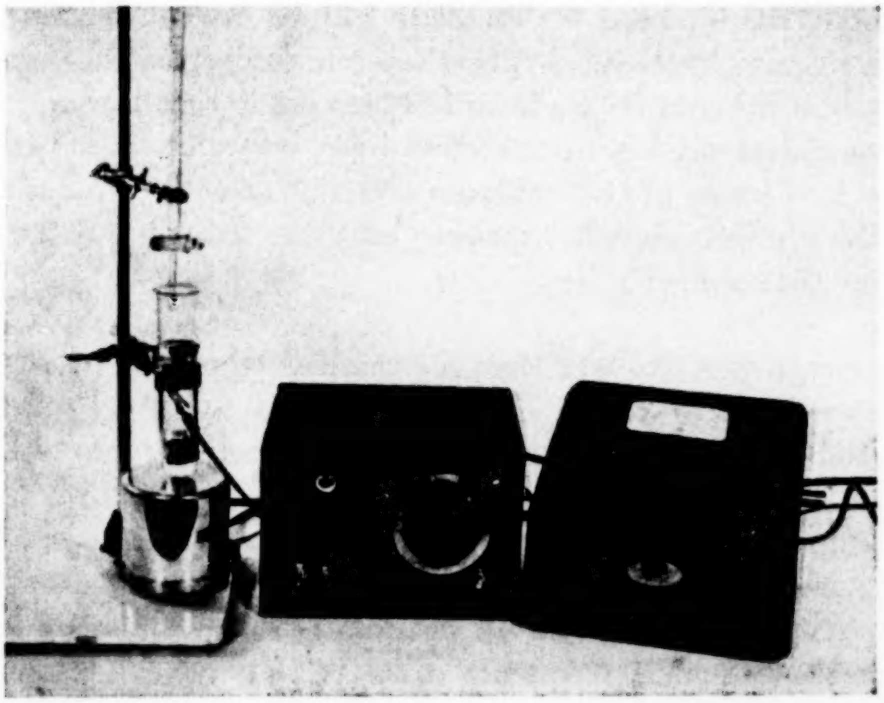

Fig. 2. Complete titration apparatus.

Jacks are provided for the measurement of the grid bias voltage with an external voltmeter. The position of variable capacitor C_1, a 100 mmfd semi-circular variable capacitor, is indicated on a 4-inch dial with vernier. In a titration any change in the effective capacitance in the titration cell circuit is compensated for by an equal and opposite change in the capacity of C_1. C_2, a 400 mmfd

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variable capacitor in parallel with C_1, allows a titration to be started at a convenient setting of C_1 with various types of titration cells. Each division of the dial of C_1, readable to tenths by means of the vernier, corresponds to about 1 mmfd.

Changes in the effective conductance in the titration cell circuit are measured as changes in the grid bias of the oscillator tube as indicated by the electron-ray tube and measured by a sensitive external voltmeter. R_1 allows the magnitude of the grid bias measured by the external voltmeter to be diminished by a constant amount of from 0 to 22 volts. This allows the use of a lower range on the voltmeter for titrations where bias does not change much. This feature was used by HALL.

The apparatus has sockets for crystals having ½- and ¾- inch pin spacing wired in parallel so that either type of crystal may be used. Standard 1¼-inch 4-prong plug-in coils are used. Thus the frequency of the oscillator can be changed simply by plugging in the appropriate coil and crystal.

It was found that a warm-up period of several hours before use minimizes drift due to thermal variations in the apparatus. A timer was set to turn on the instrument in advance so that it was ready for operation when needed.

Titration cells

A cell adapter consisting of variable capacitors and single-pole double-throw switches in a metal cabinet permitted various types of cells to be conveniently used with this titrimeter[2]. For titrations in the dilute concentration ranges cells similar to that described by HALL AND GIBSON were used[7]. This cell employs two metal bands, one above the other, around a glass tube (Fig. 2). The titration cell circuit of this type of cell is primarily affected by changes in the conductance of the solution contained in it. Continuous magnetic or air stirring can be used.

For measurements in the high concentration regions the cells were of narrow glass tubing. Metal bands again served as external electrodes. The sample solution was contained in a beaker in which the glass tube was immersed. After each increment of titrating reagent was added to the sample, the solution was thoroughly stirred, a portion was drawn up into the glass tubing and its effective conductance or capacitance measured by the high-frequency method. The liquid was again returned to the bulk solution and the process repeated.

Temperature control

Since the conductivity of aqueous solutions is dependent on the temperature and increases rapidly with rise in temperature, some type of temperature regulation was desirable. Moreover, in any conductance-loss type of instrument, the changes in amplitude of the oscillator, which are plotted versus concentration, are the result of changes in energy dissipated as heat in the resistive solution in the titration cell. This effect results in a rise in the temperature of the solution in the titration cell and was studied by FORMAN AND CRISP[5].

With the larger diameter test-tube titration cells satisfactory temperature regulation was obtained by making the lower electrode a thin copper jacket or simply wrapping copper tubing around one of the metal electrodes. This electrode was grounded and constant-temperature water was circulated through it (Fig. 3). For the narrow tubing titration cells the beaker was surrounded by a glass jacket through which constant-temperature water was pumped. Since the active electrode was removed from the bulk of the solution and the measurements were taken rapidly, this arrangement was satisfactory.

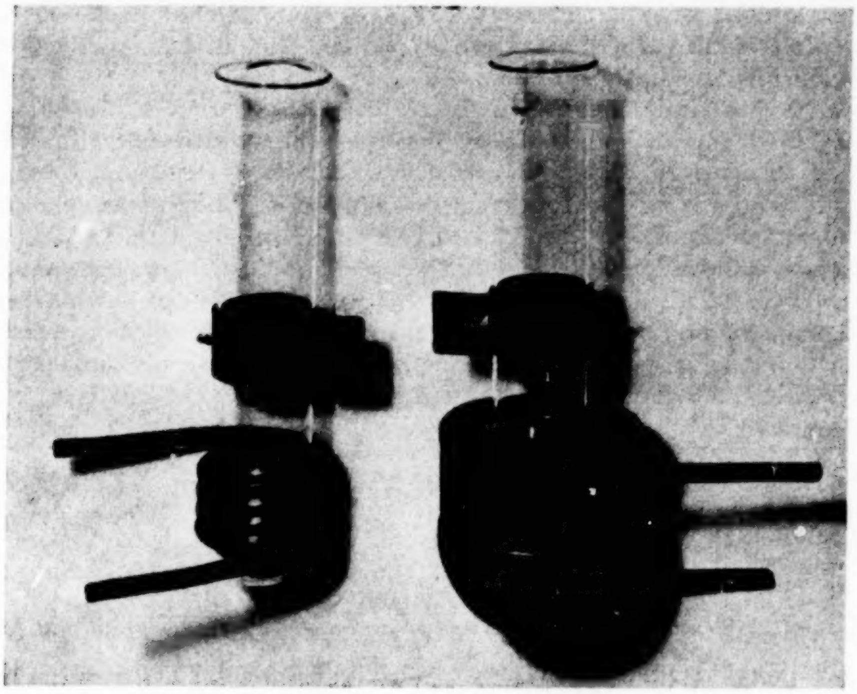

Fig. 3. Thermostated cell for highly conductive solutions.

Measurements of change in effective capacity

Effective capacity changes can be measured by the method used by BENDER, FISCHER and HALL[1,4,6]. A suggested alternate procedure involves adjusting C_1 to reproduce a certain grid bias voltage, indicated by the external voltmeter. In this method an arbitrary value on the voltmeter scale, usually about one-fourth of maximum grid bias, is selected as a reference point. This is shown as P in Fig. 4. Decreasing the capacity of variable capacitor C_1 causes the 6V6 tube to fall into oscillation. The capacitor is then adjusted until the voltmeter measuring grid bias reads this arbitrary value. The capacitor setting corresponding to this arbitrary grid bias value can be approached from either side and is very sharp since a slight change in capacitance causes a large change in grid bias voltage in this region. This method is faster and less tedious than the method used by BENDER, FISCHER and HALL, where the variable capacitor is slowly rotated until the circuit falls into oscillation, indicated by the sudden closing of the electron-ray tube. After adjustment of the variable capacitor until the arbitrarily chosen grid bias value is obtained, the dial reading is taken. These readings are made after each addition of titrating agent.

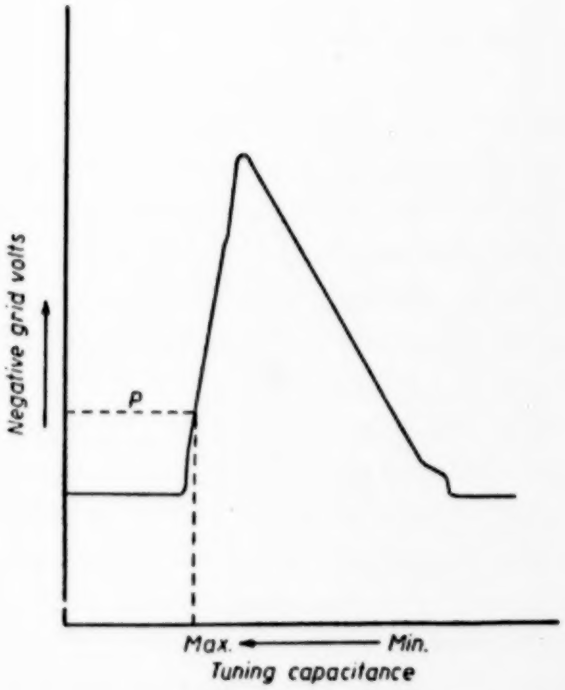

Fig. 4. Tuning curve of a crystal oscillator.

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Measurements of change in effective conductance

Changes in the effective conductance in the titration cell circuit are indicated by changes in the grid bias of the oscillator tube as indicated roughly by the electron-ray tube and measured by the external voltmeter. After each addition of titrating reagent, C_1 is adjusted to maximum grid bias voltage (resonance) and voltmeter readings are taken. Where changes in effective conductance are small, R_1 can be adjusted so that the external voltmeter reads zero or some small value. A lower meter range can then be used, resulting in greater sensitivity. For extreme sensitivity it is possible to use a pH meter, for example a Beckman model H pH meter, as a vacuum tube voltmeter. This has a 400 mV scale.

But in general it is not necessary to use a vacuum tube voltmeter as the external meter. A very high input impedance is not needed, since in effect the meter is in parallel with the 47,000 ohm grid bias resistor in the circuit. Good results have been obtained using standard volt-ohm-milliammeters for external meters. Simpson model 260 and Triplett model 630 meters have been used successfully. Both have a D.C. sensitivity of 20,000 ohms/volt. Thus, on a 50-volt range these meters have a resistance of 1,000,000 ohms, which in parallel with the 47,000 ohm grid bias resistor has negligible effect on the operating characteristics of the oscillator. Furthermore, vacuum tube voltmeters, especially line operated meters, show some drift, and this can be avoided by the use of sensitive conventional voltmeters.

Response curves

The difference between measuring changes in effective capacitance and conductance is easily seen by comparing the response curves of both methods. The response curve is a plot of the property measured by the high-frequency titrimeter versus the nor-

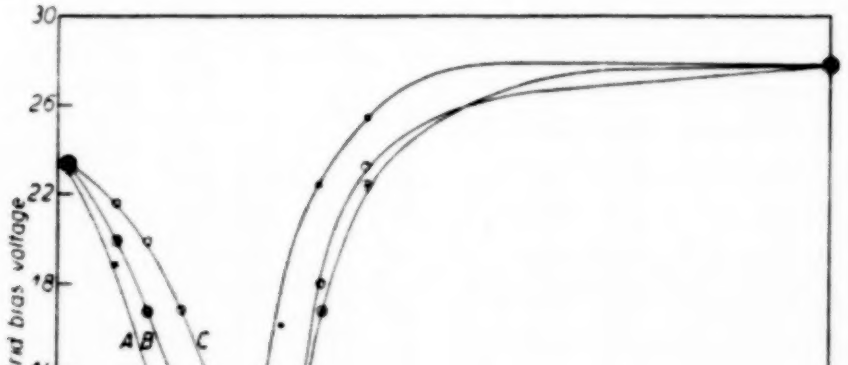

Fig. 5. Effect of electrode separation distance on high-frequency response curves. Nine-mm flint glass tubing. 2.5-cm Aluminium foil electrodes.
A. 30-cm Electrode separation distance.
B. 46-cm Electrode separation distance.
C. 61-cm Electrode separation distance.

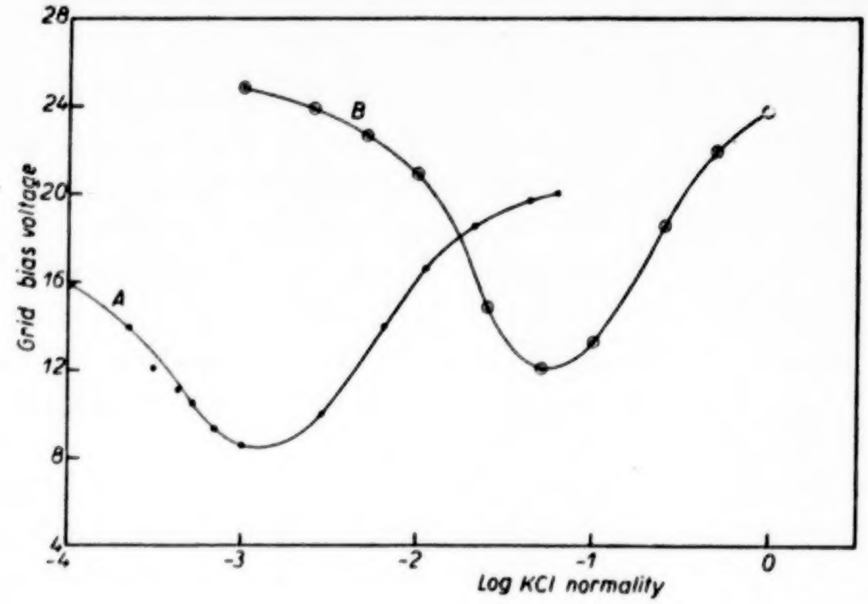

Fig. 6. Effect of cell diameter on high-frequency response curves.
A. 40-mm Glass tubing.
B. 13-mm Glass tubing.

mality or electrolytic conductance of the sample solution. Measurements of changes in effective capacity in the titration cell circuit, when plotted against concentration or specific conductance, display an S-shaped response curve; measurements of effective conductance changes yield a U-shaped curve. Only in the vicinity of the inflection point of the S-shaped curve or in the regions on either side of the minimum in the U-shaped curve is the instrument response sensitive to concentration changes.

Since the useful concentration regions of the U-shaped curves are wider than those of the S-shaped ones, this limitation is less severe for measurements of effective changes. Moreover, it has been found[3] that by progressively varying the electrode separation distance, for a given cell tube and sample solution, (Fig. 5) or varying the diameter of the glass vessel, for a constant electrode length and electrode separation distance (Fig. 6) the useful concentration regions of the response curves can be shifted over a wide range.

Titration curves

Fig. 7 illustrates the type of titration curves obtained with this high-frequency titration apparatus. Curve A represents the titration of $0.2N$ sodium hydroxide with $1N$ hydrochloric acid; curves C and D show the titration of $0.1N$ nitric acid with $0.25N$ sodium metasilicate. In these acid-base titrations the plotted end-points agreed quite closely with theory. Curve B illustrates a precipitation reaction, the titration of $0.1N$ silver nitrate with $0.1N$ potassium chloride.

Superficially these high-frequency curves resemble conductometric titration plots, but there are apparent differences. In the conductometric method the portion of the curve near the end-point is usually rounded due

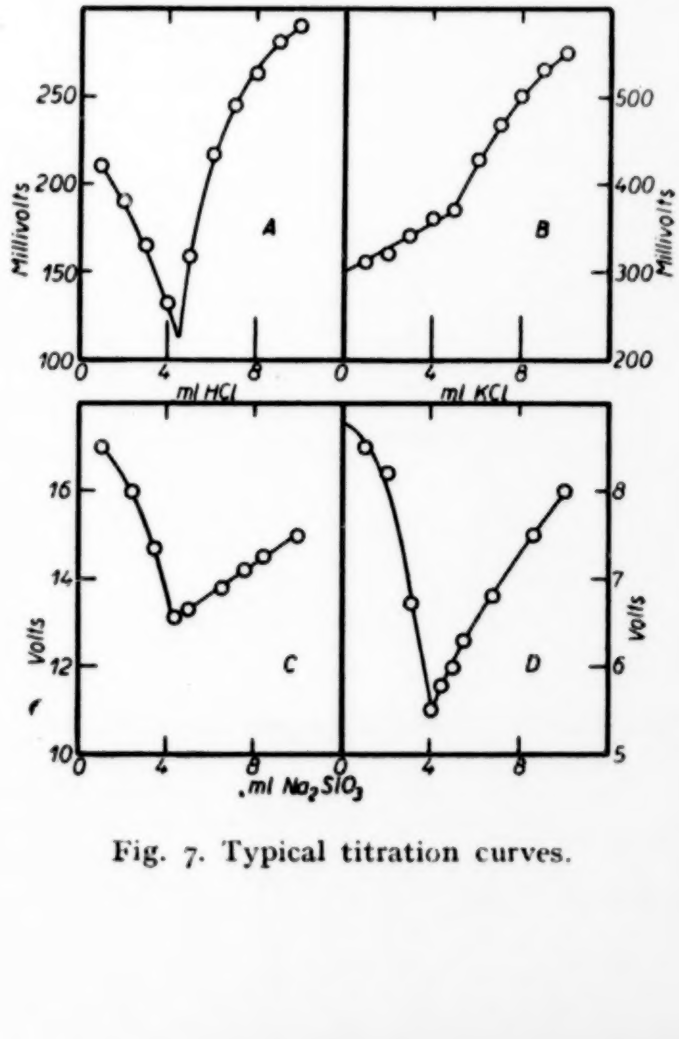

Fig. 7. Typical titration curves.

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to solubility, hydrolysis or dissociation of the reaction product. The significant points are those removed from the end-point where these phenomena are suppressed. In these high-frequency titration curves measurements removed from the equivalence point can be neglected. It is in the region near the equivalence point that the plots are linear. These points, therefore, determine the end-point.

SUMMARY

A high-frequency titrimeter which responds to either effective capacitance or to effective conductance changes in the titration cell circuit is described. The instrument is simple, inexpensive and reliable. An easy, yet accurate, method of measuring effective capacitance changes is used. Typical titration curves are given. Some novel methods of temperature control are presented including the use of the electrodes themselves as a means of regulating the temperature of the solution.

RÉSUMÉ

Un titrimètre à haute fréquence, répondant aux variations, soit de capacitance effective, soit de conductance effective lors d'une titration, est décrit. L'appareil est simple, peu coûteux et sûr. Une méthode, facile et cependant précise, permet de mesurer les variations de capacitance effective. Des courbes de titrations typiques sont données. Quelques méthodes nouvelles de contrôle de température sont présentées, comprenant l'emploi des électrodes elles-mêmes pour régler la température de la solution.

ZUSAMMENFASSUNG

Es wird ein Hochfrequenz-Titrimeter, welches Variationen, sei es der effektiven Kapazitanz, sei es der effektiven Konduktanz, während einer Titration entspricht, beschrieben. Der Apparat ist einfach, billig und sicher. Es ist eine einfache und dennoch präzise Methode, um die Variationen der effektiven und gebrauchten Kapazitanz zu messen. Einige neue Methoden für die Temperaturkontrolle werden vorgeschlagen, welche die Verwendung der Elektroden selbst, um die Temperatur der Lösung zu regulieren, vorsehen.

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THE POLAROGRAPHIC BEHAVIOUR OF SOME ELEMENTS IN CONCENTRATED CALCIUM CHLORIDE SOLUTION

V. THE DETERMINATION OF CHROMIUM IN THE PRESENCE OF NICKEL

by

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INTRODUCTION

In previous papers in this series some problems associated with polarography in concentrated solutions were discussed[1] and studies of the polarographic behaviour of a number of metals in $5M$ calcium chloride solution were reported [2,3]. During the course of this work it was shown that, for satisfactory polarography, solutions of chromic chromium must contain at least $3M$ calcium chloride ($6M$ chloride ion) and must be heated to 90-100° C to ensure that the chromic chloride complex species present has the required constitution.

In the base electrolyte employed ($5M$ calcium chloride) it was not possible to separate the steps due to chromium and nickel, either by complexing or pH adjustment and in the method developed for the determination of trace metal impurities in calcium metal[4], a polarographic determination of the combined nickel and chromium content was therefore made. The concentration of nickel was then determined on a separate aliquot by an independent method and the value obtained was used to determine the chromium concentration.

Further work on the polarography of chromium has led, rather unexpectedly, to a means of eliminating the interference of nickel with the chromium determination and hence, to a polarographic method for the determination of both these elements.

All polarography described in this paper was carried out at 25° C on a Cambridge photographic polarograph and all half-wave potentials are quoted on the European sign convention. On this convention the potential of the saturated calomel electrode (S.C.E.) has been taken as $+0.246$ volts versus the normal hydrogen electrode (N.H.E.).

EXPERIMENTAL

Whereas previous work has been devoted to the determination of impurities in calcium metal, the present work was undertaken to provide a more general method for the determination of microgram amounts of chromium. The object of the initial experiments was therefore to provide a base electrolyte which would contain the necessary concentration of chloride and at the same time ensure that all the chromium present was in the trivalent state. It was considered that this would be provided by a mixture of calcium chloride and hydroxylamine hydrochloride. A solution of $5M$ calcium chloride was therefore prepared by dissolving AnalaR quality calcium carbonate in hydrochloric acid and 6*M* hydroxylamine hydrochloride was prepared from Judex analytical reagent quality material. Standard solutions of chromium and nickel chlorides were also prepared from the purest sources available.

A series of 10 ml solutions was prepared containing 100 microgram per ml chromium in mixed base electrolytes of calcium chloride and hydroxylamine hydrochloride of various concentration ratios. Polarography of these solutions showed that in 6*M* hydroxylamine hydrochloride no chromium step was obtained, but that in a base solution which was 6.4*M* with respect to chloride and 4.2*M* with respect to hydroxylamine the results were satisfactory. In a medium which was 5.9*M* with respect to chloride ion the chromium step was sometimes much smaller than expected.

In view of these results it was decided to employ a concentration of 7*M* chloride ion and to reduce the amount of hydroxylamine to that necessary to maintain the chromium present in the trivalent state. In accordance with the recommendations in a previous paper[2] the solutions were heated at about 90 °C in a water bath to ensure that the composition of the chloride complex was only that most satisfactory for polarography. A series of solutions was prepared as follows:

Volumes of the standard chromium solution were added to 3 ml portions of 1*M* hydrochloric acid in 50 ml beakers followed by 6.0 ml 5*M* calcium chloride and 1.2 ml 6*M* hydroxylamine hydrochloride. Each mixture was gently heated on a hot plate until the volumes were reduced to about 6 ml. They were then transferred to 10 ml graduated flasks and made up to volume with water. An aliquot of each solution was deoxygenated and polarographed, when chromium steps of half-wave potential -0.47 volts versus the mercury pool were obtained. The heights of these steps were measured by the intersection method previously described[5]. The results obtained were used to prepare the calibration graph shown in Fig. 1.

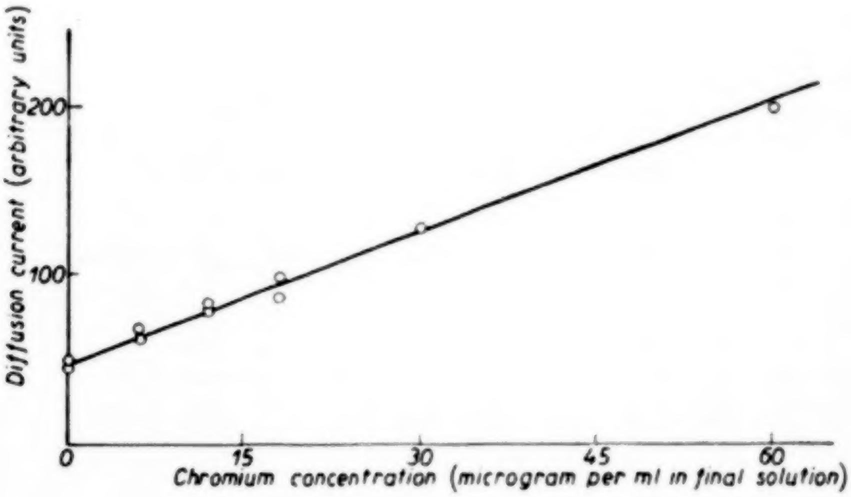

Fig. 1. Step height against chromium concentration (base electrolyte not purified by electrolysis).

Examination of Fig. 1 indicated that, although the relationship between step height and chromium concentration was linear the „reagent blank" was almost equivalent to 18 microgram chromium per ml. It was considered necessary to reduce this in order to obtain more accurate figures at the lower levels. Experiments were therefore carried out designed to devise a method for purifying the reagents. Recrystallisation of the hydroxylamine hydrochloride produced no significant improvement. Filtration of the calcium carbonate solution at pH 1 was no more successful. The calcium chloride solution was therefore electrolysed at a stirred mercury cathode which was maintained at -1.6 volts versus a saturated calomel electrode. This treatment reduced the blank to an equivalent of 3 micrograms per ml in the final solution.

During these experiments it was found that, if the solutions were evaporated to a volume of less than 6 ml the chromium step height obtained was smaller than expected. It was considered that this was due to loss of hydrochloric acid, which would have the effect of reducing the overall chloride concentration and increasing the pH of the solution. It was known that both these factors were unfavourable to the formation of good reduction steps and some hydrochloric acid was therefore added before the evaporation of the solution was carried out.

It was found that, under these conditions, over-evaporation of the solution did not affect the chromium step height.

Determination of chromium in the presence of nickel

It was already known[2] that nickel and lead interfere with the determination of nickel in $5M$ calcium chloride solution and a means of elimination of the interference of lead has already been described[4].

Calibration curves for chromium and nickel were prepared exactly as already described, but using the purified calcium chloride. The results are shown in Fig. 2, from which it will be seen that the nickel step height was only 6% of that obtained with the same concentrations of chromium. A series of experiments was therefore carried out to study the effect of varying amounts of nickel on the chromium recoveries. The results of duplicate determinations (A and B) are given in Table I. The calcium chloride used for these experiments was not purified by electrolysis.

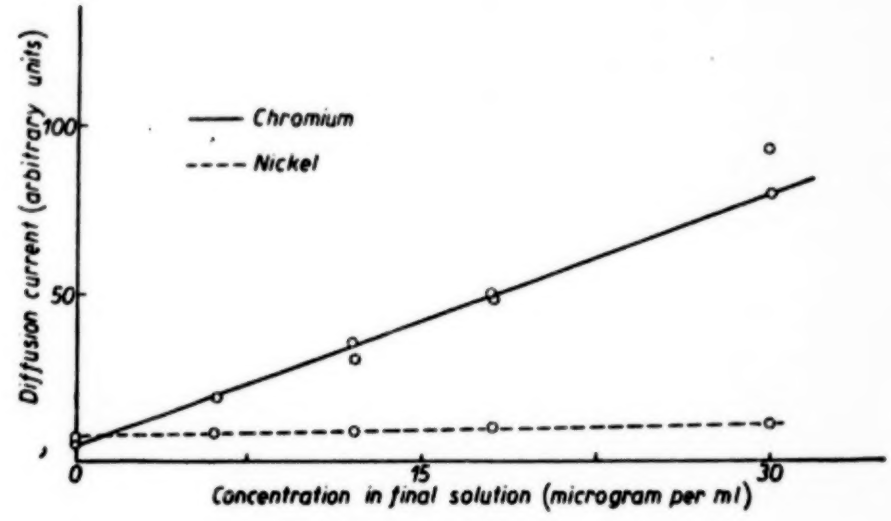

Fig. 2. Chromium and nickel calibration graphs.

TABLE I

Added concentration		*Step height**		*Chromium recovered microg/ml*	
Chromium microg/ml	*Nickel microg/ml*	*A*	*B*	*A*	*B*
0	0	52**	52**	—	—
6	60	75	77.5	10	11
12	18	81	77	12	11
18	12	99	96	19	18
30	30	130	136	30	31.5
60	6	205	210	58	59

* All steps heights are quoted in arbitrary units and have been corrected to that which would be obtained on the maximum sensitivity of the polarograph employed.

**This step height represents the "blank" on the reagents.

Finally a series of solutions containing the same concentration of nickel (30 microg per ml) in various concentrations of chloride ion was prepared and polarographed. The results are presented in Table II. For ease of comparison the "blank" step height has been subtracted in each case. This "blank" was separately determined at each chloride concentration.

TABLE II

Chloride concentration	*Step height at -0.47 volts*
7.4*M*	5
8.3*M*	20
9.3*M*	60.5
10.3*M*	81.5
11.3*M*	78.5

Determination of chromium and nickel in calcium metal

No major modifications of the method already described for the determination of trace impurities in calcium metal[4] are needed. In addition to the determination in 5*M* calcium chloride (10*M* chloride) an aliquot, prepared similarly but treated with hydroxylamine hydrochloride and diluted to give a final concentration of 7.4*M* chloride (0.4*M* hydroxylamine) is necessary. From the former solution the combined nickel and chromium wave is obtained, while the latter provides the chromium value alone. The concentrations of both may therefore be obtained from appropriate calibration graphs. Recoveries of added chromium obtained are shown in Table III. The blank due to the sample content has been subtracted from the results.

TABLE III

Sample No.	*Microg/ml added*		*Chromium recovered (microg/ml)*
	Chromium	*Nickel*	
1	6	15	7
2	10.5	15	10
3	15	15	16
4	21	30	21
5	28.5	60	28

DISCUSSION

The polarography of chromium and nickel in 5*M* calcium chloride solution has already been studied by us[1,2] and it was recommended that at least 3*M* calcium chloride should be employed as the base electrolyte and the pH should not exceed 3.5. The present work confirms these conclusions, as even in the 5.9*M* chloride solution, employed at one stage of the work, the chromium step was sometimes much smaller than expected. This failure is presumably due to the incomplete formation of that chloride complex which reduces at -0.47 volts versus the mercury pool and the figure of 6*M* chloride, given as necessary for the satisfactory polarography of chromic chromium must be regarded as critical.

The absence of a reduction step for nickel in the 7.4*M* chloride solution was unexpected and the results given in Table II were therefore obtained to study the effect of variation in chloride concentration. Examination of these results shows that the size of the nickel step increases with increasing chloride concentration to a maximum at 10.3*M*. This must occur when all the nickel is present as the chloride complex which reduces more reversibly than the hexaquo nickel ion. The decrease in step height when the chloride concentration is increased to 11.3*M* must be due to the increase in viscosity of the medium with consequent decrease in the diffusion coefficient. It has been reported elsewhere that the optimum concentration of calcium chloride for maximum polarographic sensitivity is between 4 and 5*M*[6]. The step height of 5 obtained with the solution of concentration 7.4*M* with respect to chloride shows that only about 6% of the nickel is present as the chloride complex mentioned above. Thus a minimum concentration of 10*M* chloride must be recommended for the satisfactory polarography of nickel if the reversible reduction at -0.47 volts is to be used.

It will be seen from Table I that only in the case where the nickel-chromium ratio was 10:1 were very high chromium recoveries obtained. In this case the apparent recovery was about 180%, but in all other cases the enhancement was smaller. Our experience has indicated that in the case of calcium metal and other materials where these impurities have entered during processing in steel plant and containers, the concentration of nickel very rarely exceeds that of chromium. Table I shows that when their concentrations are equal the enhancement of the chromium concentration is about 6%. This is considered to be negligible at the level of the determination. If, however, the nickel-chromium ratio greatly exceeds 2:1 enhancement becomes appreciable and allowance must be made for it.

ACKNOWLEDGEMENT

Acknowledgement is made to the Chief Scientist, British Ministry of Supply, for permission to publish this paper.

SUMMARY

Further studies on the polarography of trivalent chromium in concentrated calcium chloride solution are described. Details are given of a chloride-hydroxylamine base electrolyte (7.4*M* with respect to chloride) in which chromium may be determined directly in the presence of nickel. This method is not applicable if the nickel-chromium ratio is large. Results are presented and certain theoretical aspects are discussed.

RÉSUMÉ

De nouvelles études ont été effectuées sur la polarographie du chrome(III) dans des solutions concentrées de chlorure de calcium. Des détails sont donnés sur l'utilisation du chlorhydrate d'hydroxylamine comme électrolyte de base (7.4*M*); le chrome peut alors être dosé directement en présence de nickel. Cette méthode n'est pas applicable si le rapport nickel-chrome est grand. Des résultats sont présentés et certains aspects théoriques sont discutés.

ZUSAMMENFASSUNG

Es wurden neue Untersuchungen angestellt über die Polarographie des Chrom(III) in gesättigten Kalzium-Chloridlösungen. Es werden Einzelheiten über die Verwendung von Hydroxylamin-chlorhydrat als Basis-Elektrolyt (7.4*M*) gegeben. Das Chrom kann direkt in Gegenwart von Nickel bestimmt werden. Diese Methode ist nicht anwendbar wenn das Verhältnis Nickel-Chrom gross ist. Es werden Resultate vorgelegt und theoretische Gesichtspunkte diskutiert.

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COMMUNICATION

ANALYTICAL SECTION

International Union of Pure and Applied Chemistry

ANALYTICAL SECTION IUPAC ELECT OFFICERS

The Analytical Section of the International Union of Pure and Applied Chemistry elected four new members to its Section Committee. These are Mr. Samuel E. Q. Ashley of General Electric Company (Louisville, Kentucky, U.S.A.), Dr. Roland Belcher of the University of Birmingham (England), Prof. Gerold Schwarzenbach of the University of Zurich (Switzerland), and Dr. Fredrick D. Tuemmler of the Shell Development Company (Emeryville, California, U.S.A.); these memberships are for a term of four years except that of Mr. Ashley which is a two-year term.

The election results were declared after examination of a letter ballot of the Section members at the meeting of the Section Committee at Zurich on July 21 and 27, during the XVIIIth Conference of the IUPAC held at the Swiss Federal Institute of Technology. During the same meeting, Dr. Tuemmler was elected Secretary of the Section by the Section Committee, a post to be held until 1959. He succeeded Mr. Ashley who held the office since 1949. In its meeting on July 21, the Section Committee expressed by rising vote of thanks, its great indebtedness to Mr. Ashley for all the work which he has done on behalf of the Section.

The President of the Section, Prof. I. M. Kolthoff of the University of Minnesota (Minneapolis, U.S.A.), the Vice President, Mr. R. Clark Chirnside of the General Electric Company (Wembley, England), and the Secretary, form the Executive Committee of the Section. The remaining four members of the Analytical Section Committee are Prof. G. Duyckaerts of the University of Liège; Prof. C. J. van Nieuwenburg of the Technische Hoogeschool (Delft, The Netherlands), Prof. Lars Gunnar Sillén of the Royal Institute of Technology (Stockholm, Sweden) and Prof. Dr. Michael K. Zacherl of the Tierärztliche Hochschule (Vienna, Austria). The terms for these six members expire in 1957.

The members whose term expired this year are Prof. Fritz Feigl of Rio de Janeiro (Brazil), Dr. J. I. Hoffman of the U.S. National Bureau of Standards (Washington, D.C.) and Prof. Dr. P. E. Wenger of the École de Chimie de l'Université (Geneva, Switzerland). Prof. Wenger served as Vice President of the Union from 1951 to 1955 and was one of the leaders in the reorganization of the Analytical Section in the period since 1948.

MORE ON LISBON CONGRESS

In connection with the 1956 International Analytical Congress at Lisbon being held under the patronage of the Analytical Section of the Union, it was decided that all papers submitted essentially should be new or novel contributions; review papers would be discouraged. In the interest of securing papers at as high a level of scientific interest as possible, the national adhering bodies of the Union have been requested to screen the papers submitted from their respective countries.

The Lisbon Analytical Congress, the XVth Congress of the IUPAC is being arranged by an Organizing Committee of Chemists in Portugal, of which Prof. Dr. Pierre A. Laurent, of the Instituto Superior Técnico, Avenida Rovisco Pais, is Secretary-General. The Congress will be divided into the following Sections: (1) Microchemical Methods, (2) Biological Methods, (3) Electrical Methods, (4) Optical Methods, (5) Radiochemical Methods, (6) Organic Complexes, (9) General, and (10) Standardization of Methods and Miscellaneous Applications. Persons interested in having further information regarding the Congress should write to Prof. Laurent at the above address.

ACTIVITIES OF COMMISSIONS OF ANALYTICAL SECTION

All of the Commissions of the Analytical Section have been very active during the past year, two of them reporting to the Union on pending publications. The Commission on Analytical Reactions, headed by Prof. Jean Gillis (Rijksuniversiteit Gent, Belgium) reported that the monograph on colorimetry of inorganic compounds prepared by Prof. Clément Duval (National

Center of Scientific Research, Paris, France) has just been published under the patronage of the Analytical Section.

The Commission on Equilibrium data, headed by Prof. L. G. SILLÉN (Royal Institute of Technology, Stockholm, Sweden) has collected a great number of published equilibrium data. To date, Prof. J. BJERRUM (University of Copenhagen, Denmark) has prepared a complete set of tables of stability constants of inorganic complexes and chelate compounds (of the order of a few thousand), covering literature up to 1953. After some further editing and making the data complete to the end of 1955 by Profs. SCHWARZENBACH and SILLÉN, these very valuable tables will be published in 1956, by the Chemical Society of London under sponsorship of the IUPAC. This Commission is also engaged in making a critical compilation, with representative diagrams, of the solubility of hydroxides, hydrous oxides, slightly soluble sulfates, metal sulfides, and silver halides.

The Commission on Electrochemical Data, headed by Dr. ROGER G. BATES (U.S. National Bureau of Standards, Washington D.C., U.S.A.) is compiling selected electrochemical data of analytical importance, specifically of oxidation-reduction potentials at various ionic strengths in several electrolytes; to date, data for 52 of the elements is complete and work on the remainder will begin in the fall. A systematic collection of selected values of polarographic properties is being compiled; a standard data form has been adopted for the uniform presentation of data (half-wave potential, diffusion current), experimental conditions (solvent, pH, maximum suppressor, type of microelectrode), reference and explanatory remarks. A critical evaluation has been completed of the accuracy and limitations of the several methods by which dissociation constants have been obtained. Since the solvent medium plays a fundamental part in acid-base dissociation, the constants are being arranged according to solvent; some 80 original articles have been reviewed and constants for 50 compounds collected.

The Commission on Optical Data, headed by Prof. G. DUYCKAERTS (University of Liège, Belgium) is engaged in the preparation of a critical compilation of numerical data on absorption spectra and extinction coefficients of complexes used in analytical chemistry; some two hundred compounds have been covered to date. The Commission will also assist in the coordination of information on molecular spectroscopy (infrared) of analytical interest.

The Commission on Terminology and Expression of Analytical Results, under the guidance of Prof. ROBERT J. FORBES (Bataafsche Petroleum Mij, The Hague, The Netherlands), has brought to completion a draft on Format of an Analytical Method; the Commission is cooperating with ISO/TC 47 in this project to develop a uniform recommendation on the writing of commercial test methods for national and international use. Similar cooperation is being maintained with ISO/TC 12 on the subject of uniform symbols and units.

The Commission on Microchemical Techniques under the guidance of Prof. Dr. MICHAEL K. ZACHERL (Tierärztliche Hochschule, Vienna, Austria) has completed a survey of microchemical techniques and in some 25 different countries to ascertain profitable subjects for standardization. Work is now starting on the preparation of international standards of microchemical apparatus and listing of preferred notations (units) of measurement with special reference to microtechniques.

In a joint meeting of the Analytical and of the Physical-Chemical Sections, overlapping of functions and cooperation between Commissions was discussed. Plans were laid for the basis of cooperation between the Commission on Electrochemical Data in the Analytical Section and the Commission on Electrochemistry of the Physical-Chemical Section. A new Commission on Molecular Spectroscopy in the Section of Physical Chemistry is contemplated, but the Commission on Optical Data will remain charged with the collection and coordination of information of analytical value.

At present, there are 54 members in the Analytical Section of the Union, including the Section Committee and its Commissions, representing 17 adhering countries; Austria, Belgium, Czechoslovakia, Denmark, England, Finland, France, India, Italy, The Netherlands, Northern Ireland, Spain, Sweden, Switzerland, the United States of America, and West Germany.

A PROPOSED STRUCTURE FOR THE COPPER(II) SALTS OF α-ACYLOIN OXIMES

by

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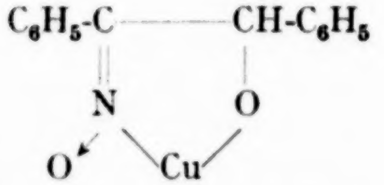
One of the best reagents for the detection and determination of copper (II) is the α-isomer of benzoin oxime, C_6H_5-CH(OH)-C(NOH)-C_6H_5, introduced into analytical chemistry by FEIGL in 1923[8]. FEIGL, SICHER AND SINGER[9] established that the ability to form green, water insoluble copper (II) salts is very likely a general property of α-isomers of acyloin oximes. It has been found[8, 11, 12] that benzoin oxime acts towards copper (II) ions as a "dibasic acid", *i.e.* the hydrogen atoms of both the oxime and the hydroxy groups are replaced by one copper atom. The copper (II) salt of benzoin oxime is characterized by insolubility in most organic solvents and by its inertness towards dilute ammonium hydroxide. Insolubility in ammonium hydroxide, however, is not common to all copper (II) salts of acyloin oximes[9].

Although it has been well established that for analytical purposes the copper (II) salt of benzoin oxime can be represented by the formula:



the solubility relationships of the compound cannot be satisfactorily reconciled with this structure.

In the present investigation the behavior of copper (II) salts of some acyloin oximes towards various amines was examined in order to study the unusual solubility relationships of these compounds.

The copper (II) salts of the α-acyloin oximes given in Table I were included in the study.

EXPERIMENTAL

A. Organic Preparations

All temperatures are uncorrected and were recorded with a N. B. S. certified thermometer.

The acyloin oximes prepared were obtained as white crystalline solids unless otherwise stated. From the behavior of these acyloin oximes towards copper (II) it is concluded that in all cases only the α-isomer was isolated.

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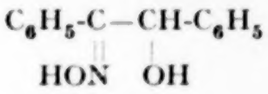
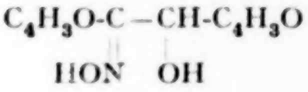
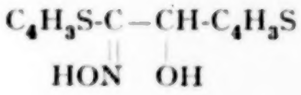
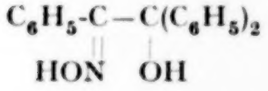
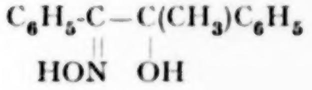
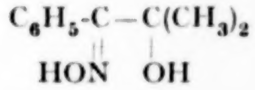
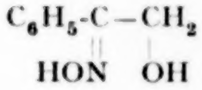
TABLE I

ACYLOIN OXIMES INVESTIGATED

Name of compound	*Formula of compound*
Benzoin oxime	 $C_6H_5\text{-}\underset{\underset{\text{HON}}{\parallel}}{C}-\underset{\underset{\text{OH}}{\mid}}{CH}\text{-}C_6H_5$
2,2'-Furoin oxime	 $C_4H_3O\text{-}\underset{\underset{\text{HON}}{\parallel}}{C}-\underset{\underset{\text{OH}}{\mid}}{CH}\text{-}C_4H_3O$
2,2'-Thenoin oxime	 $C_4H_3S\text{-}\underset{\underset{\text{HON}}{\parallel}}{C}-\underset{\underset{\text{OH}}{\mid}}{CH}\text{-}C_4H_3S$
Phenylbenzoin oxime	 $C_6H_5\text{-}\underset{\underset{\text{HON}}{\parallel}}{C}-\underset{\underset{\text{OH}}{\mid}}{C}(C_6H_5)_2$
Methylbenzoin oxime	 $C_6H_5\text{-}\underset{\underset{\text{HON}}{\parallel}}{C}-\underset{\underset{\text{OH}}{\mid}}{C}(CH_3)C_6H_5$
α-Hydroxy*iso*butyrophenone oxime	 $C_6H_5\text{-}\underset{\underset{\text{HON}}{\parallel}}{C}-\underset{\underset{\text{OH}}{\mid}}{C}(CH_3)_2$
α-Hydroxyacetophenone oxime	 $C_6H_5\text{-}\underset{\underset{\text{HON}}{\parallel}}{C}-\underset{\underset{\text{OH}}{\mid}}{CH_2}$

Benzoin oxime. The commercially available product, supplied by City Chemical Corporation, was recrystallized from benzene; m.p. 149-150°, m.p. reported[2] 150-151°.

2,2'-*Furoin oxime.* Freshly distilled furfural was condensed with potassium cyanide according to HARTMAN AND DICKEY[11]. The furoin obtained was oximated with an excess of hydroxylamine hydrochloride in pyridine and methyl alcohol solution. The furoin oxime was finally recrystallized from a mixture of absolute alcohol and petroleum ether "B"; m.p. 157-158°, m.p. reported[3] 160-161°.

2,2'-*Thenoin oxime.* This preparation was carried out as described by CARDON AND LANKELMA[5]. The final product had a slight brown discoloration, while the above authors report a white product; m.p. 151-152°, m.p. reported[5] 142-143°.
Anal. Calcd. for $C_{10}H_9NO_2S_2$: C, 50.2; H, 3.8; N, 5.9; S, 26.8. Found: C, 50.3; H, 3.9; N, 5.7; S, 26.6.

Phenylbenzoin oxime Phenylbenzoin was prepared by the addition of phenylmagnesium bromide to benzil according to ACREE[1]. The oxime was obtained by the action of hydroxylamine hydrochloride in pyridine and methyl alcohol solution. The product was purified by recrystallization from a mixture of benzene and petroleum ether "B"; m.p. 148-149.5°.
Anal. Calcd. for $C_{20}H_{17}NO_2$: C, 79.2; H, 5.7; N, 4.6. Found; C, 79.4; H, 5.9; N, 4.7.

Methylbenzoin oxime. Methylbenzoin was synthesized following the method described by ROGER[18]; methylmagnesium iodide was added to benzil. The oxime was prepared and purified in the same manner as the phenylbenzoin oxime; m.p. 121-122°.
Anal. Calcd. for $C_{15}H_{15}NO_2$: C, 74.7; H, 6.3; N, 5.8. Found; C, 74.8; H, 6,4; N, 5.8.

α-Hydroxyisobutyrophenone oxime: *α*-Hydroxy*iso*butyrophenone was prepared by the addition of 0.2 moles of acetone cyanohydrin to one mole of phenylmagnesium bromide in ether solution. After the addition of the cyanohydrin some ether was distilled, replacing it with dry benzene until the temperature of the vapor reached 60°. Stirring under reflux was continued for 6 hours and after standing overnight the mixture was hydrolyzed and the product extracted with benzene. The benzene was flashed off and the residue distilled under reduced pressure. The fraction boiling between 120-130° at 12 mm was collected. Weight: 11.4 g or 35%.

The oxime was prepared by refluxing for 6 hours the ketol obtained with a filtered solution of

hydroxylamine hydrochloride (6.0 g)and potassium hydroxide (5.0 g) in methyl alcohol (100 ml). The product obtained was crystallized twice from a mixture of benzene and petroleum ether "B"; m.p. 114-115°, m.p. reported[4] 106°.
Anal. Calcd. for $C_{19}H_{13}NO_2$: C, 67.0; H, 7.3; N, 7.8. Found: C, 67.3: H, 7.2; N, 7.7.

α-Hydroxyacetophenone oxime. The oxime was prepared by refluxing for 2 hours a mixture of α-hydroxyacetophenone (5 g) in methyl alcohol (20 ml) with a solution of hydroxylaminehydrochloride (3.0 g) and potassium hydroxide (2.7 g) in water (20 ml). The mixture was extracted with ether and this solution dried over anhydrous sodium sulfate. The residue obtained after evaporation of the ether was crystallized from a mixture of benzene and petroleum ether "B", m.p. 60-70°. Recrystallization from water which contained some ammonium hydroxide gave a product of m.p. 69-70°, m.p. reported [14] 70°.

B. Determination of solubilities

The copper salts of acyloin oximes which are formed in ammoniacal solution were tested for their solubilities in a series of amines. The solubility determinations were performed in the following manner: To ten drops of the acyloin oxime solution contained in a test tube, two drops of an ammoniacal copper(II) solution were added. After the addition of 1 ml of water and thorough shaking, the mixture was centrifuged. The residue obtained was suspended in 1 ml of 95% alcohol and the suspension separated by centrifugation. To the drained residue, 1-2 ml of the amine was added and the mixture homogenized by shaking. After standing for a few minutes, the mixture was centrifuged again.

Solubility terms used in this study: A copper salt was designated as "insoluble" when the supernatent amine was either colorless or so faintly colored as to make a decision difficult. A copper salt was designated as "slightly soluble" (sl. sol.) when the supernatent amine was distinctly colored, but no change in the amount of solid could be observed. A copper salt was designated as "partly soluble" (partly sol.) when a noticeable quantity of the solid dissolved. A copper salt was designated as "soluble" when no noticeable amount of solid remained undissolved.

The following solutions were employed in this study:
1) Ammoniacal copper (II) solution: 0.1*M* copper (II) sulfate (c.p. grade) in 1.0*M* ammonium hydroxide. pH of this solution was 9.8.
2) Acyloin oxime solutions: 0.1*M* solution of the acyloin oxime in 95% ethyl alcohol.

The amines employed were either c.p. grade or were purified by distillation. When discoloration of the c.p. grade amine had occured they were also distilled. The following list gives the sources of the materials as well as the boiling ranges of the purified amines:

Ammonium hydroxide: 27% solution in water. Baker's Analyzed.
Methylamine: 25% solution in water. Eastman Kodak.
Ethylamine: 33% solution in water. Eastman Kodak.
*iso*Propylamine: Eastman Kodak.
Aniline: Eastman Kodak, redistilled. Boiling point of fraction 184-185°.
Ethylenediamine: 95-100%. Eastman Kodak.
Diethylamine: The Matheson Co.
Piperidine: Eastman Kodak. The product was dried over solid potassium hydroxide and distilled. Boiling point of fraction: 105-107°.
Methylaniline: Eastman Kodak, redistilled. Boiling point of fraction: 195-196°.
Dimethylaniline: Eastman Kodak.
Triethylamine: Eastman Kodak.
Pyridine: Baker's Analyzed.
α-Picoline: Eastman Kodak, redistilled. Boiling point of fraction: 127-130°.
γ-Picoline: Eastman Kodak, redistilled. Boiling point of fraction: 143-154°.
Quinoline: Eastman Kodak. The product was dried over solid potassium hydroxide and distilled. Boiling point of fraction: 234-235°.
"Versene": 0,2*M* aqueous solution of disodium salt of ethylenediamine tetraacetic acid. The disodium salt used was supplied by the Alrose Chemical Co. under the trade name of "Sequestrene NA2".

The colors of the copper salts dissolved in the amines were usually green, varying from a yellow-green to a deep grass-green. Exceptions were the solution colors in ammonium hydroxide, methylamine, ethylenediamine, and versene. In these instances the colors observed were blue, indicating the formation of the respective copper (II) ammine complexes.

The results are collected in Table II.

TABLE II

SOLUBILITY OF COPPER SALTS OF ACYLOIN OXIMES IN DIFFERENT AMINES

Amine	*Cu-Benzoin oxime*	*Cu-Thenoin oxime*	*Cu-Furoin oxime*	*Cu-Phenylbenzoin oxime*	*Cu-Methylbenzoin oxime*	*Cu-α-Hydroxyiso-butyrophenone oxime*	*Cu-α-Hydroxy-acetophenone oxime*
Ammonium hydroxide	sl. sol.	sl. sol.	soluble	soluble	sl. sol.	partly sol.	partly sol.
Methylamine	sl. sol.	sl. sol.	partly sol.	soluble	insoluble	insoluble	partly sol.
Ethylamine	sl. sol.	insoluble	insoluble	soluble	insoluble	insoluble	partly sol.
*iso*Propylamine	sl. sol.	insoluble	insoluble	soluble	insoluble	insoluble	partly sol.
Aniline	insoluble	insoluble	insoluble	soluble	insoluble	insoluble	insoluble
Ethylenediamine	soluble	soluble	soluble	soluble	soluble	soluble	soluble
Diethylamine	sl. sol.	insoluble	insoluble	soluble	insoluble	insoluble	insoluble
Piperidine	insoluble	insoluble	insoluble	soluble	sl. sol.	insoluble	sl. sol.
Methylaniline	insoluble	insoluble	insoluble	soluble	insoluble	insoluble	insoluble
Dimethylaniline	insoluble	insoluble	insoluble	soluble	insoluble	insoluble	insoluble
Triethylamine	insoluble	insoluble	insoluble	soluble	insoluble	insoluble	insoluble
Pyridine	partly sol.	insoluble	partly sol.	soluble	insoluble	sl. sol.	sl. sol.
α-Picoline	partly sol.	insoluble	partly sol.	soluble	insoluble	sl. sol.	sl. sol.
γ-Picoline	partly sol.	insoluble	partly sol.	soluble	insoluble	sl. sol.	sl. sol.
Quinoline	partly sol.	insoluble	partly sol.	soluble	insoluble	sl. sol.	sl. sol.
"Versene"	partly sol.	sl. sol.	partly sol.	partly sol.	sl. sol.	partly sol.	soluble

C. *Analysis of copper salts*

The copper content of the copper (II) salts of methylbenzoin oxime, thenoin oxime, α-hydroxy-*iso*butyrophenone oxime and α-hydroxyacetophenone oxime was determined by precipitating a known quantity of copper from ammoniacal solution with excess oxime. The compounds obtained were thoroughly washed to remove excess reagent and dried to constant weight at 125-130°. With methylbenzoin oxime and thenoin oxime the excess reagent had to be removed by washing with hot ethanol.

Table III reproduces the results. Although the amounts of copper methylbenzoin oxime and copper thenoin oxime obtained are somewhat high, there is little doubt that the ratio of copper to oxime is in all cases 1:1.

TABLE III

ANALYSIS OF COPPER SALTS OF ACYLOIN OXIMES

Acyloin oxime	*Weight of copper* (*grams*)	*Weight of copper salt* *found* (*grams*)	*calculated* (*grams*)
2,2'-Thenoin oxime	0.0244	0.1185	0.1155
	0.0251	0.1215	0.1188
Methylbenzoin oxime	0.0278	0.1337	0.1325
	0.0283	0.1378	0.1349
α-Hydroxy*iso*butyrophenone oxime	0.0317	0.1209	0.1201
	0.0325	0.1227	0.1231
α-Hydroxyacetophenone oxime	0.0244	0.0817	0.0817
	0.0253	0.0852	0.0847

DISCUSSION

The present investigation extended the study of the characteristic acyloin oxime grouping, —C(NOH)—C(OH)<, towards copper (II) to four compounds not previously investigated; *i.e.* 2,2'-thenoin oxime, methyl benzoin oxime, α-hydroxy*iso*butyrophenone oxime, and α-hydroxyacetophenone oxime. These compounds showed the same reactivity as benzoin oxime, the most readily available compound containing the above grouping. All compounds form green, water insoluble copper (II) salts in which the ratio of metal to organic component is 1 : 1.

The behavior of the copper salts of these acyloin oximes as well as the copper salts of benzoin oxime, 2,2'furoin oxime and phenylbenzoin oxime was tested towards various amines. FEIGL[8] was the first to note the unusual behavior of the copper (II) salts of acyloin oximes towards ammonia. Surprisingly these compounds are insoluble in ammonium hydroxide provided that the acyloin is derived from an aromatic aldehyde or an aliphatic aldehyde with more than four carbon atoms. Exceptions to this rule are the copper salts of phenyl- and benzylbenzoin oxime. FEIGL explained the insolubility in ammonia by assuming the copper (II) compounds to be inner complex salts.

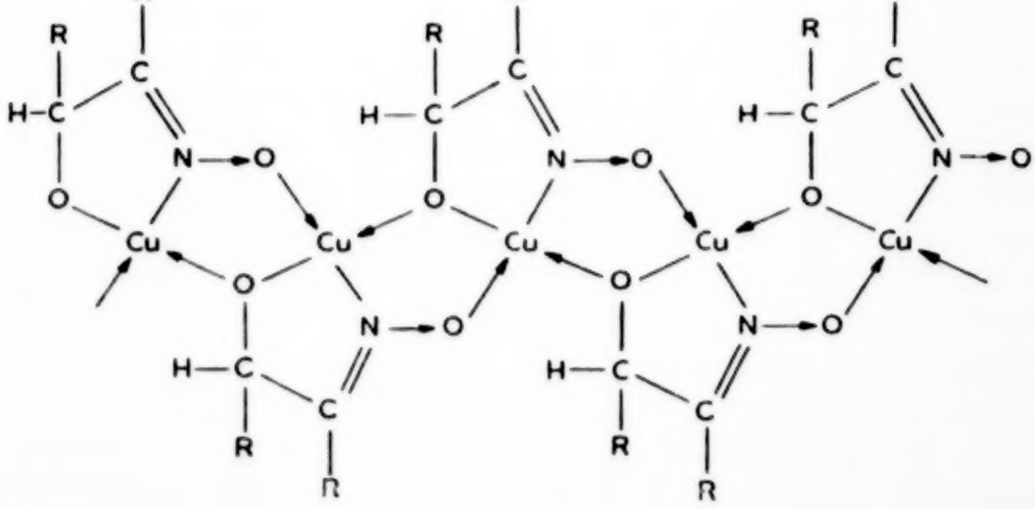
DUBSKY AND LANGER[6] postulate a dimeric formula for copper (II) benzoin oxime as a basic salt. Thermal analysis of the copper salt[7] showed it to be anhydrous above 60° C. LANGER[13] proposed a dimeric structure which calls for a coordination number of 3 for the copper. Ray and Sen[17] conclude from magnetic susceptibility studies that the copper in the copper benzoin oxime compound has a coordination number of 4. They assume for this copper salt an unending chain structure similar to the structure of anhydrous palladium (II) chloride. Steric considerations make their structure rather unlikely.

The insolubility in ammonia of copper salts of acyloin oximes cannot be satisfactorily explained by considering these compounds as inner complex salts. Evidence against this postulate is afforded by the solubility behavior of the copper salts of the oximes of α-hydroxy*iso*butyrophenone and α-hydroxyacetophenone.

The behavior of the copper salts of acyloin oximes can best be interpreted by assuming a polymeric structure for these compounds. Based on this assumption the insolubility in ammonia can be explained without recourse to coordination to phenyl radicals or multimembered aliphatic radicals. The central copper atom would be shielded from an attack by the ammonia molecule by hydrophobic groups such as phenyl or multimembered aliphatic radicals. The solubility of the copper salts of phenyl- and benzylbenzoin oxime could be explained by the inability of these acyloin oximes to form such polymers because of the size of the organic component. The possibility that the solubility of these compounds in ammonia is to be ascribed to the fact that the hydroxy group in these two acyloin oximes is attached to a tertiary carbon atom can be ruled out from the behavior of the copper salts of methylbenzoin oxime and α-hydroxyisobutyrophenone oxime.

According to Palit and McBain[16] and Palit[15] compounds which contain both hydrophobic and hydrophilic groups are soluble in liquids or mixtures of liquids which contain both these groupings. The behavior of the copper salts of acyloin oximes affords some evidence in favor of this postulate. The copper salts studied showed excellent solubility in ethylene diamine, a solvent for the organic component as well as a strong coordinating agent for copper ion. From the blue solution color it can be inferred that decomposition of the copper (II) salts takes place. Pyridine and its homologues which also fulfill the above criteria are fair solvents for copper (II) acyloin oximes.

A structure which seems to fit all available data is given below.



Unfortunately no suitable solvent was found in which molecular weight determinations could be carried out.

SUMMARY

The behavior of the copper (II) salts of the α-isomers of some acyloin oximes towards a series of selected amines was examined in order to study the unusual solubility relationships which these copper salts exhibit towards ammonium hydroxide. The insolubility in ammonium hydroxide of these copper salts of acyloin oximes has been attributed to their being inner complex salts. Evidence is presented which is contra y to this view. Based on the solubilities of the copper (II) salts investigated, a polymeric structure for copper (II) acyloin oximes is proposed.

The study included the following α-isomers of acyloin oximes: benzoin oxime, 2,2'-furoin oxime, phenylbenzoin oxime, methylbenzoin oxime, 2,2'thenoin oxime, α-hydroxy*iso*butyrophenone oxime, and α-hydroxyacetophenone oxime. The last four compounds had not been examined previously as to their ability to form copper (II) salts.

RÉSUMÉ

Le comportement des sels de cuivre(II) des α-isomères de quelques acyloinoximes, vis-à-vis d'une série d'amines a été examiné. On a pu ainsi étudier les solubilités anormales que présentent ces sels de cuivre dans les solutions d'hydroxyde d'ammonium. Cette solubilité avait été attribuée au fait que les sels de cuivre forment avec ces oximes des complexes internes, ce qui n'est en réalité pas le cas. En se basant sur les solubilités de ces sels de cuivre(II) une structure polymère est proposée.

Cette étude a été effectuée sur les composés suivants: benzoinoxime, 2,2' furoinoxime, phénylbenzoinoxime, méthylbenzoinoxime, 2,2'-thénoinoxime, α-hydroxy*iso*butyrophénonoxime et α-hydroxyacétophénonoxime. Ces 4 derniers n'avaient pas encore été examinés quant à leur faculté de former des sels de cuivre(II).

ZUSAMMENFASSUNG

Das Verhalten der Kupfer(II) salze der α-Isomeren von einigen Acyloinoximen gegenüber einer Reihe von Aminen wurde untersucht. Auf diese Weise konnte man die abnormalen Löslichkeiten, welche diese Kupfersalze in Ammoniumhydroxyd-Lösungen aufweisen, untersuchen. Diese Löslichkeit ist der Tatsache zugeschrieben worden, dass die Kupfersalze mit diesen Oximen interne Komplexe bilden, was in Wirklichkeit nicht der Fall ist. Gestützt auf die Löslichkeiten dieser Kupfer(II) salze wird eine polymere Struktur vorgeschlagen. Diese Untersuchung wurde mit den folgenden Substanzen ausgeführt: Benzoinoxim, 2,2'-Furoinoxim, Phenylbenzoinoxim, Methylbenzoinoxim, 2,2'-Thenoinoxim, α-Hydroxy*iso*butyrophenonoxim und α-Hydroxyacetophenonoxim. Diese vier letzten Substanzen sind bisher noch nicht untersucht worden, in Bezug auf ihre Fähigkeit, Kupfer(II) salze zu bilden.

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ÉTUDE DE LA PHÉNYL-2 OXINE ET DE SES CHÉLATES

I. PRÉPARATION ET PROPRIÉTÉS DE LA PHÉNYL-2 OXINE

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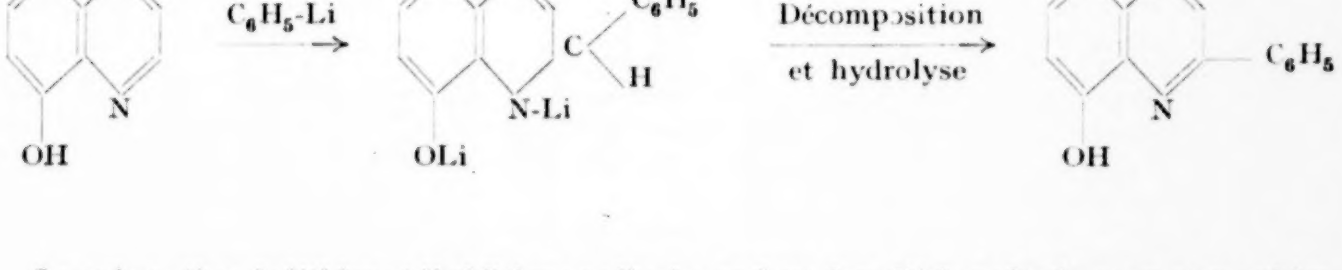
On sait qu'il est possible de modifier les propriétés de l'oxine (hydroxy-8 quinoléine) en compliquant la molécule par l'introduction de substituants variés: des études récentes sur divers dérivés alcoylés ont mis en évidence l'intérêt particulier de la position α; il a été établi[1,2,3,4] que l'introduction d'un radical en cet endroit empêche la formation de certains chélates, en particulier celui d'aluminium. En examinant de plus près les propriétés d'un nouveau dérivé 2-substitué, on pouvait s'attendre à ce que la comparaison des résultats avec ceux des études antérieures permette d'intéressantes observations quant à l'action des substituants sur les propriétés du réactif et de ses chélates.

Nous nous proposons donc de présenter ici l'essentiel du travail[5] que nous avons effectué sur le dérivé α-phénylé de l'oxine: la phényl-2 hydroxy-8 quinoléine, ou phényl-2 oxine.

Préparation de la phényl-2 oxine

Parmi les modes d'obtention possibles de ce composé, le plus expéditif consiste à partir de l'oxine en mettant à profit la propriété que présentent les composés organolithiens de se fixer en position 1-2 sur les bases pyridiques ou quinoléiques:



La préparation du lithien et l'addition sur l'oxine se font dans l'éther absolu et en atmosphère inerte; il n'est cependant pas indispensable d'opérer sous courant d'azote. Il est préférable d'utiliser un défaut d'oxine: en partant de 0.4 at-g (2.8 g) de lithium, 0.2 mole (31.5 g) de bromobenzène, et 0.05 mole (7.3 g) d'oxine, nous avons ainsi obtenu 0.026 mole (5.7 g) de produit brut, soit un rendement de l'ordre de 50%.

L'oxine non transformée est éliminée par un entraînement à la vapeur d'eau au pH correspondant à son point isoélectrique (7.5); puis la phase organique est extraite à l'éther et distillée sous vide: on recueille la phényl-2 oxine brute sous forme d'une huile visqueuse, colorée (de jaune pâle à rouge plus ou moins foncé), que l'on recristallise dans le méthanol.

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Polymorphie

Tandis que DOEBNER ET FETTBACH[6] qui avaient préparé la phényloxine par une autre voie (décarboxylation de l'acide α-phénylcinchonique) indiquent un point de fusion de 59° C, IRVING, BUTLER ET RING[4] obtiennent par la méthode de DOEBNER ET FETTBACH un produit fondant à 85.5° C et, par action de l'organolithien sur l'oxine, un produit fondant à 58-59° C. En utilisant trois méthodes différentes, nous n'avons jamais obtenu de produit fondant à 85.5° C mais le point de fusion de nos premiers produits était 59° C et ensuite, quelque soit le mode opératoire, ce point de fusion a toujours été 72° C. Il apparaît donc que cette phényl-2 oxine existe au moins sous trois formes polymorphes, dont la plus stable est vraisemblablement celle qui fond à 72° C.

Propriétés principales

La phényl-2 oxine (P.M. = 221.25) est un solide blanc: P.F. = 59 ou 72 ou 85.5° C, P.E.$_{16\,\mathrm{mm}}$ $\approx$ 230° C; la forme fondant à 72° C cristallise en lamelles ayant la forme de losanges.

Elle donne un picrate: P.F. = 159° C; par recristallisation dans le méthanol contenant de l'acide chlorhydrique ou de la soude caustique nous avons obtenu le chlorhydrate (aiguilles jaunes, P.F. = 190-191° C) et le sel de sodium (jaune foncé, P.F. = 170° C avec décomposition).

La phényl-2 oxine n'est pas entraînable à la vapeur d'eau, contrairement à l'oxine ou à la méthyl-2 oxine. Elle est soluble dans les solvants organiques usuels, mais très peu soluble dans l'eau; elle se dissout mieux en milieu aqueux fortement acide ou basique, en donnant des solutions jaunes.

Comme l'oxine elle présente la faculté de former avec un certain nombre d'ions métalliques des complexes internes ou chélates.

Spectre d'absorption dans l'ultra-violet

En solution *dans le cyclohexane* la phényl-2 oxine présente un spectre analogue à celui de l'oxine, avec deux bandes d'absorption d'intensités très différentes. Les valeurs suivantes ont été observées pour les longueurs d'onde et les coefficients d'extinction moléculaire aux maximums: λ = 271-272 mμ, ε = $46.6 \cdot 10^3$ et λ = 322-324 mμ, ε = $5.0 \cdot 10^3$.

Les résultats publiés par PHILLIPS[7] pour divers dérivés méthylés de l'oxine montrent que l'introduction d'un groupement CH_3 en position 2 produit un déplacement hypsochromique marqué de la bande λ = 320 mμ de l'oxine, alors que la bande λ = 242 mμ est peu affectée. L'influence de la position du substituant apparaît d'ailleurs par le fait que le spectre de la méthyl-4 oxine est très semblable à celui de l'oxine elle-même.

Dans le cas de la phényl-2 oxine nos résultats comme ceux de PHILLIPS mettent en évidence un effet différent: c'est alors la bande λ = 320 mμ de l'oxine dont la position est peu affectée, alors que la bande $\lambda = 242$ mμ subit un déplacement bathochromique important.

Pour chacune des deux bandes de la phényl-2 oxine la loi de Beer est suivie dans tout le domaine de concentrations étudié ($2\cdot10^{-6} < C < 1.6\cdot10^{-4}$ mole/litre).

En milieu *hydroalcoolique neutre à 50° G.L.* on retrouve à peu de choses près le même spectre: $\lambda = 270$ mμ, $\varepsilon = 46.0\cdot10^{3}$ et $\lambda = 321$-323 mμ, $\varepsilon = 6.0\cdot10^{3}$.

Là encore, la loi de Beer est suivie dans tout le domaine exploré; nous avons ainsi le moyen de mesurer des concentrations en phényl-2 oxine allant de 50 à 0.5 mg/litre.

Toutes ces mesures ont été faites au spectrophotomètre Beckman D.U., avec des cuves de 1.00 cm.

Application:
mesures de solubilité de la phényl-2 oxine

De l'eau distillée ou des mélanges hydroalcooliques à teneur variable en alcool ont été saturés de phényloxine par agitation prolongée, et la mesure spectrophotométrique de la concentration a été faite après avoir amené la composition de la solution à 50° G.L.

Dans l'eau pure il se dissout, par litre, à 22 ± 1° C, 3.75 mg (soit $1.7\cdot10^{-5}$ mole) de phényloxine. Celle-ci est donc nettement moins soluble que l'oxine (de l'ordre de $5\cdot10^{-3}$ mole/litre) et que les dérivés méthylés (d'après PHILLIPS[7]: méthyl-2: $2.5\cdot10^{-3}$; méthyl-3 et diméthyl-2.3: $\sim 5\cdot10^{-4}$ mole/litre vers 30° C).

En milieu hydroalcoolique la solubilité croît lentement d'abord, puis beaucoup plus rapidement lorsque la teneur en alcool atteint 30 à 40° G.L., comme le montre la courbe de la Fig. 1.

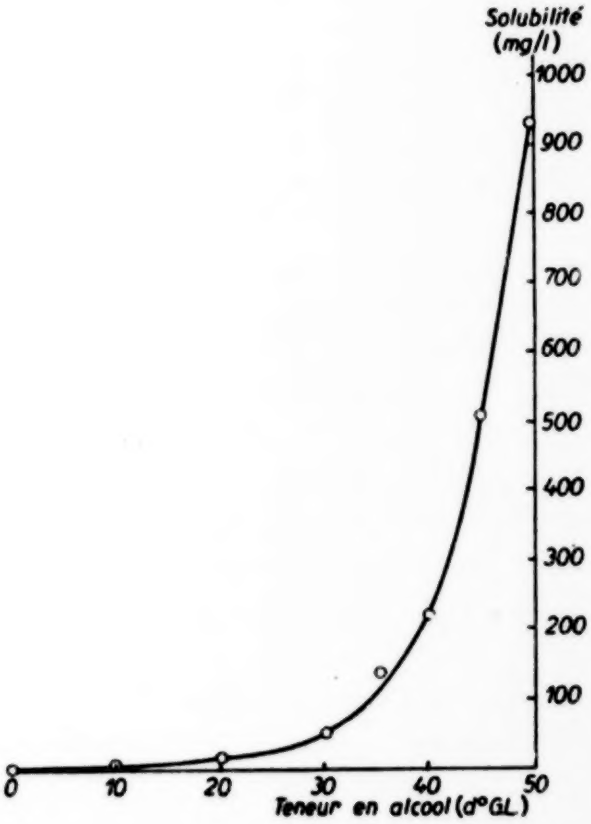

Fig. 1. Solubilité de la phényl-2 oxine en fonction de la teneur en alcohol.

Spectre ultraviolet en fonction du pH

Les Figs. 2 et 3 représentent les spectres d'absorption dans l'ultraviolet pour la phényl-2 oxine en milieu acide et en milieu alcalin. Chaque courbe a été obtenue à l'aide d'une solution à 10 mg par litre dans un milieu hydroalcoolique à 20° G.L. tamponné.

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Chacun de ces réseaux de courbes représente le passage progressif d'une forme de phényloxine à une autre, soit lorsque le pH croît: de la forme ionique acide (ions phényl-oxinium H_2PhOx^+) à la forme moléculaire neutre (phényloxine HPhOx; Fig. 2); puis, de cette dernière à la forme ionique basique (ions phényloxinate $PhOx^-$; Fig. 3). Les courbes extrêmes (à pH 1.1 et 13.7) peuvent être considérées comme les spectres d'absorption respectivement des ions H_2PhOx^+ et $PhOx^-$, alors que le spectre de la phényl-2 oxine non dissociée est donné par les courbes aux pH voisins du point isoélectrique (ou mieux dans le cyclohexane). Les caractéristiques des bandes des 3 spectres sont donc les suivantes dans le milieu considéré:

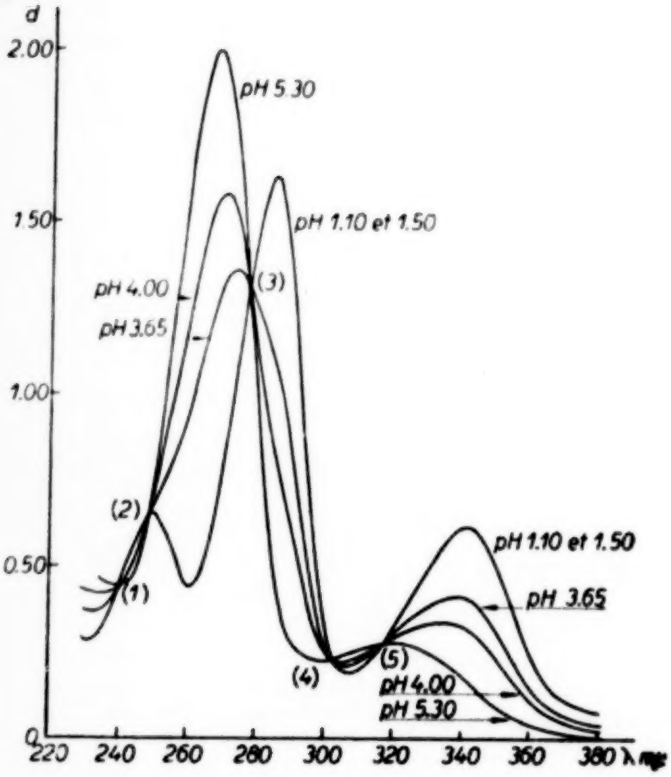

Fig. 2. Spectres d'absorption de l'ultraviolet par la phényloxine (C = 10 mg/l) en milieu hydroalcoolique 20° G.L. à différents pH (milieu acide).

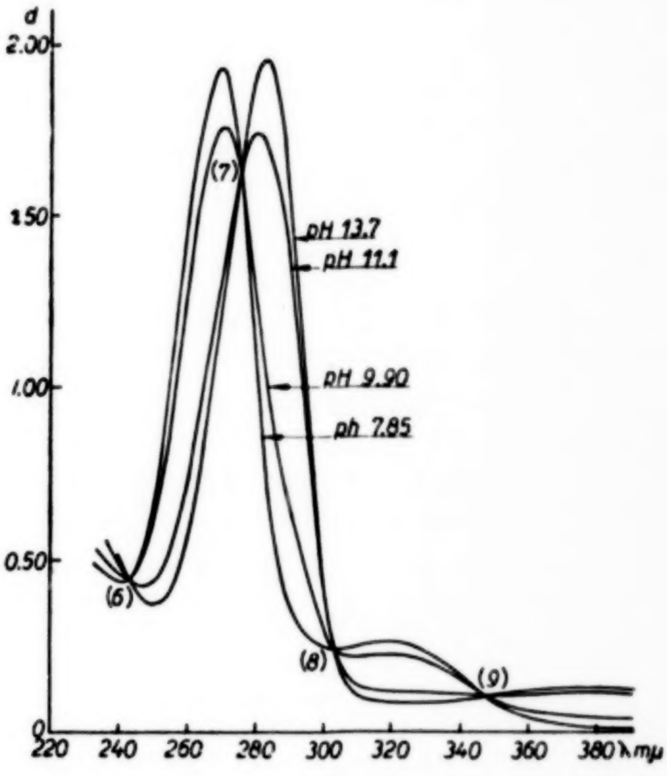

Fig. 3. Spectres d'absorption de l'ultraviolet par la phényloxine (C = 10 mg/l) en milieu hydroalcoolique 20° G.L. à différents pH (milieu alcalin).

H_2PhOx^+ :	$\lambda = 250\text{-}1$ mμ	$(\varepsilon = 14.4 \cdot 10^3)$
	$\lambda = 285$ mμ	$(\varepsilon = 35.5 \cdot 10^3)$
	$\lambda = 341\text{-}2$ mμ	$(\varepsilon = 13.7 \cdot 10^3)$
H PhOx	$\lambda = 270$ mμ	$(\varepsilon = 46.0 \cdot 10^3)$
	$\lambda = 321\text{-}3$ mμ	$(\varepsilon = 6.0 \cdot 10^3)$
Ph Ox^-	$\lambda = 283$ mμ	$(\varepsilon = 42.0 \cdot 10^3)$
	$\lambda = 387\text{-}8$ mμ	$(\varepsilon = 3 \cdot 10^3)$

Lorsqu'on acidifie ou alcalinise, le spectre est déplacé vers le visible; ce déplacement bathochromique, plus accentué pour la bande de plus grande longueur d'onde, correspond au changement de coloration des solutions (d'incolore à jaune en milieu acide et jaune orangé en milieu alcalin).

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Les spectres des formes H_2PhOx^+ et $PhOx^-$ étant différents, il est normal de ne pas retrouver le même spectre pour deux valeurs différentes du pH, l'un acide et l'autre basique. Par contre, tous ces spectres ont un certain nombre de points communs: les points isobestiques. Ces points, où se coupent toutes les courbes d'un même réseau, indiquent en général l'existence en solution de deux formes en équilibre, la concentration totale étant constante. Le Tableau I en donne les coordonnées (les numéros renvoient aux Figs. 2 et 3).

TABLEAU I

LONGUEURS D'ONDE λ mμ ET COEFFICIENTS D'EXTINCTION MOLÉCULARE ε AUX POINTS ISOBESTIQUES

	Milieu acide			*Milieu alcalin*	
No.	λ	$\varepsilon \cdot 10^{-3}$	*No.*	λ	$\varepsilon \cdot 10^{-3}$
(1)	240-2	9.5	(6)	243-4	9.8
(2)	249-50	14.2	(7)	275-6	35.6
(3)	278	28.8	(8)	303-4	5.2
(4)	302-3	5.0	(9)	347-8	2.3
(5)	316-7	6.0			

Il est curieux de noter que les points (1) et (6) d'une part, (4) et (8) d'autre part, sont très voisins, sinon confondus. Il est peu probable que cette circonstance soit fortuite: elle serait plutôt l'indication d'une certaine analogie de structure des 3 formes H_2PhOx^+, HPhOx et $PhOx^-$, hypothèse déjà formulée[8] dans le cas de l'oxine.

RÉSUMÉ

Les auteurs, qui ont préparé la phényl-2 oxine par trois méthodes différentes, ont obtenu un produit fondant à 59° C, puis, par la suite, une autre forme fondant à 72° C. L'étude des spectres d'absorption dans l'ultraviolet a été faite soit en solution cyclohexanique, soit en solution hydroalcoolique; cette étude spectrale a permis de mesurer la solubilité de la phényloxine en milieu aqueux et en présence d'alcool à concentration croissante. En représentant les spectres aux différents pH (de 1.1 à 13.7) on note un certain nombre de points isobestiques.

SUMMARY

The authors prepared phenyloxin by three different methods. They obtained a product whose melting point was 59° C and then another form melting at 72° C. Ultraviolet absorption spectra were determined in cyclohexan and in alcohol-watermixtures; from these determinations, the solubilities of phenyloxin in water and in alcohol-watermixtures of different concentrations were obtained. If ultraviolet absorption spectra are plotted for different pH values (from 1.1 to 13.7) several isobestic points are noted.

ZUSAMMENFASSUNG

Die Verfasser, die das Phenyloxin nach drei verschiedenen Methoden hergestellt haben, erhielten erst ein bei 59° C schmelzendes, später aber ein bei 72° C schmelzendes Produkt. Die Ultraviolett-Absorptionsspektren wurden in Cyclohexan und in Wasser-Alkohol-Gemischen untersucht; auf Grund dieser Spektraluntersuchung konnte die Löslichkeit des Phenyloxins in Wasser und in wässrigem Alkohol steigender Konzentration gemessen werden. Wenn man die Spektren für verschiedene pH-Werte (1.1 bis 13.7) aufzeichnet, erhält man eine Anzahl gemeinsamer Punkte, die sogenannten "points isobestiques".

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THE APPLICATION OF THIOSALTS IN ANALYSIS
IV. A NEW SCHEME OF QUALITATIVE ANALYSIS
Part A

by

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In the papers[1,2] entitled "The Application of Thiosalts in Analysis", a new scheme of qualitative analysis was put forward, based on the formation of the thiosalts of certain elements with concentrated ammonium sulphide reagent and their subsequent decomposition with excess of hydrochloric acid, for the detection of basic radicals in mixtures containing common as well as the so-called "rare" elements.

In a recent publication[3] it was shown that 1*N* sodium sulphide is a far more convenient and efficient reagent than concentrated ammonium sulphide.

In this series it is proposed to give a brief outline of the new scheme of qualitative analysis for the detection of basic radicals in mixtures containing only the common elements.

Procedure I

As the mixture is not likely to be soluble in water or dilute acids, the first step in analysis consists in evaporating the mixture with concentrated nitric acid and hydrochloric acid in such a manner that the latter is added when about 5 ml of nitric acid is left. The *aqua regia* thus formed in the intermediate stage not only ensures the complete solution of the compounds which require an oxidizing or reducing acid solvent, but completely eliminates the use of bromine water to oxidize tin from the divalent to tetravalent state. In addition to this, substances like manganese dioxide and lead peroxide which require a reducing acid solvent dissolve easily when this procedure is followed.

The residue is boiled with dilute hydrochloric acid, filtered and washed several times with hot water. The insoluble portion still left may contain AgCl, CaF_2, $CrCl_3$ (violet), $BaSO_4$, $SrSO_4$, $PbSO_4$, $Cr_2(SO_4)_3$ (anhydrous), Al_2O_3, SnO_2, Sb_2O_4, SiO_2, stannic phosphate and complex ferro- and ferricyanides. In following the procedure outlined above insoluble substances like SnS_2 (mosaic gold), HgS and $Zn_2[Fe(CN)_6]$ go completely into solution, whereas AgBr, AgI, AgCN, AgCNS, $Ag_4[Fe(CN)_6]$, $Ag_3[Fe(CN)_6]$, are all converted to AgCl. (A schematic analysis for the insolubles is given in part B of the series[4]). The mercurous salts are oxidized to the mercuric form, lead passes into the filtrate as $PbCl_2$, whereas silver forms part of the insoluble residue as AgCl respectively.

Procedure II

The acid solution containing all the basic radicals is treated with 1*N* sodium sulphide reagent in excess (add 20 ml of the reagent in excess after the acid has been neutralized), 2-4 g of ammonium acetate and 2 g of sodium carbonate. The mixture is stirred thoroughly and filtered. The precipitate is washed with distilled water, the washings being added to the filtrate. The precipitate may contain the hydroxides and sulphides, *etc.*, of metals like mercury, lead, bismuth, and the filtrate the thiosalts of arsenic, antimony, tin as well as magnesium and alkali metals. Since sodium has been introduced as an impurity from an external source this metal may be tested in a separate portion of the mixture by flame test or by any other well-known tests.

Procedure III

The solution containing the thiosalts is boiled with excess of concentrated hydrochloric acid and filtered. The concentration of the acid in the resulting mixture should be $6N$ to precipitate completely arsenic sulphide and to dissolve the sulphides of tin and antimony. Under these conditions nickel sulphide which passes down into the filtrate in the colloidal form also gets completely precipitated as nickel sulphide. The detailed analysis of the precipitate is given in Table I.

Procedure IV

To the filtrate containing tin and antimony $1N$ sodium sulphide is added in excess until the precipitate of tin and antimony sulphides which may form dissolves in excess of the reagent. The resulting solution is treated with dilute hydrochloric acid and filtered. The detailed analysis of the precipitate is given in Table II and of the filtrate in Table III.

Procedure V

The precipitate of the sulphides and hydroxides obtained in Procedure II is treated with cold $1N$ hydrochloric acid for 2-3 minutes and filtered immediately. This treatment dissolves out all the hydroxides and sulphides except those of mercury, lead, bismuth, copper, cadmium, nickel and cobalt. The filtrate contains the chlorides of iron, manganese, aluminium, chromium, zinc and also alkaline earth metals. The detailed analysis of the precipitate is given in Table IV.

Procedure VI

The filtrate from Procedure V is treated with sodium hydroxide, sodium peroxide and sodium carbonate. Boiled to decompose the excess of sodium peroxide and filtered. The precipitate may contain the hydroxides of manganese, iron as well as alkaline earth metals. The filtrate contains aluminium, zinc and chromium. The precipitate is treated as indicated in Table V and the filtrate as in Table VI.

The separation of metals into different groups according to the proposed scheme may be diagrammatically represented as follows:

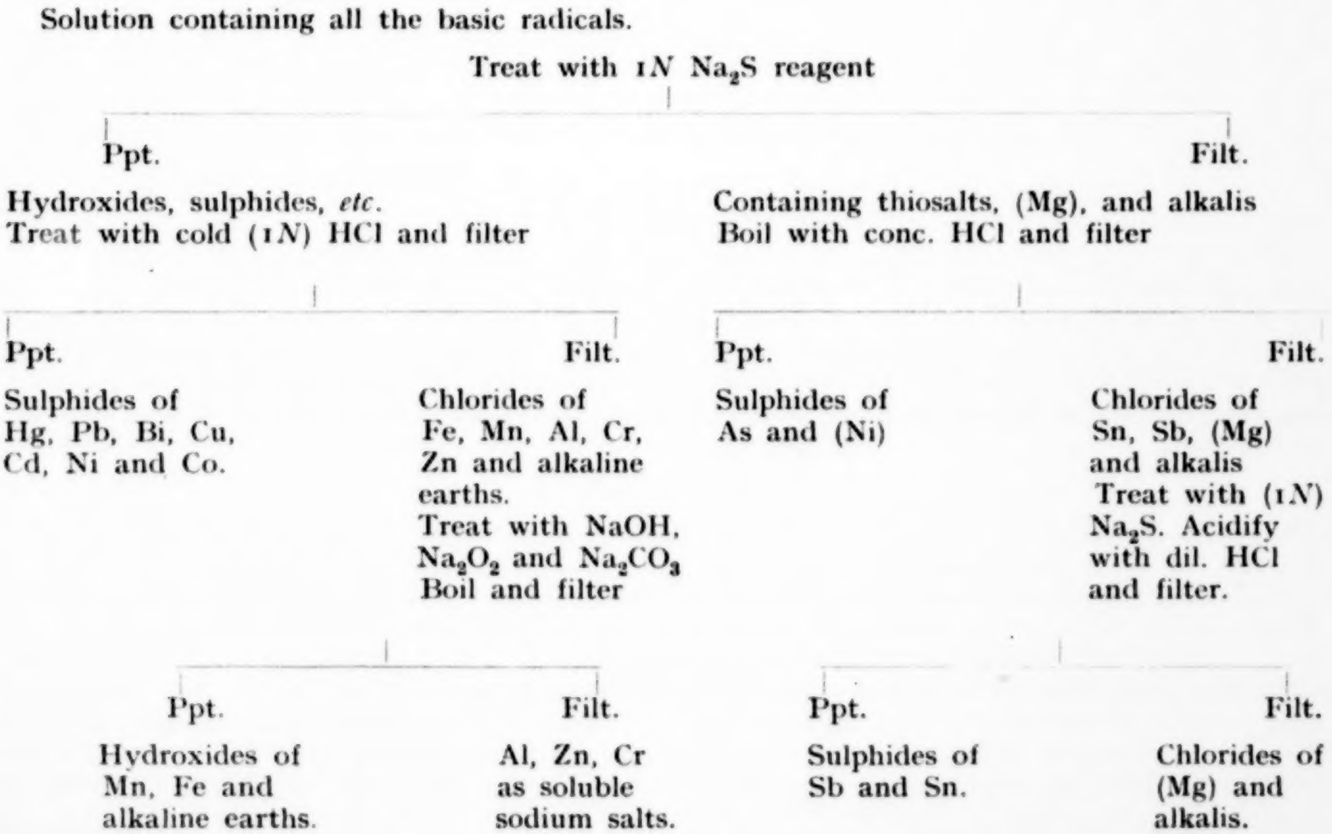
Solution containing all the basic radicals.
Treat with $1N$ Na_2S reagent
Ppt.
Hydroxides, sulphides, *etc.*
Treat with cold ($1N$) HCl and filter
Filt.
Containing thiosalts, (Mg), and alkalis
Boil with conc. HCl and filter
Ppt.
Sulphides of Hg, Pb, Bi, Cu, Cd, Ni and Co.
Filt.
Chlorides of Fe, Mn, Al, Cr, Zn and alkaline earths.
Treat with NaOH, Na_2O_2 and Na_2CO_3
Boil and filter
Ppt.
Sulphides of As and (Ni)
Filt.
Chlorides of Sn, Sb, (Mg) and alkalis
Treat with ($1N$) Na_2S. Acidify with dil. HCl and filter.
Ppt.
Hydroxides of Mn, Fe and alkaline earths.
Filt.
Al, Zn, Cr as soluble sodium salts.
Ppt.
Sulphides of Sb and Sn.
Filt.
Chlorides of (Mg) and alkalis.

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TABLE I

(Precipitate obtained in *Procedure III*)

The precipitate may contain As_2S_5 and NiS. Dissolve the precipitate in conc. HCl and a crystal of $KClO_3$. Add ammonium hydroxide in excess followed by magnesia mixture and filter. (Nickel forms a complex with ammonia and is not affected by magnesia mixture.)

Ppt. $Mg(NH_4)AsO_4$, $6H_2O$. Dissolve in dil. HCl. Add (1*N*) Na_2S in excess and acidify with conc. HCl. A yellow ppt. Shows **As**	Filt. Add dimethylglyoxime and acidify with dilute acetic acid. A red ppt. or coloration. Shows **Ni**

TABLE II

(Precipitate obtained in *Procedure IV*)

The precipitate may contain SnS_2 and Sb_2S_3.

Boil with 6*N* HCl. Treat the solution with clean iron wire, heat for a few minutes and filter.

Ppt. Sb (metal) Dissolve in HNO_3, neutralize with NaOH, add 1*N* Na_2S in excess and acidify with dil. HCl. An orange ppt. Shows **Sb**	Filt. $SnCl_2$ Add $HgCl_2$ solution. White ppt. changing to grey. Shows **Sn**

TABLE III

(Filtrate obtained in *Procedure IV*)

The filtrate may contain chlorides of Mg, K, Na and NH_4.

Add NH_4OH in excess, followed by a conc. $(NH_4)_2CO_3$ solution (better to add 2 g of $(NH_4)_2CO_3$ solid), alcohol and filter.

<table>
<tr><td rowspan="2">Ppt.
$MgCO_3(NH_4)_2CO_3$, $6H_2O$
(a) Dissolve a portion in dil. HCl. Add NH_4OH in excess and then $(NH_4)_2HPO_4$. A white ppt of $Mg(NH_4)PO_4$.
(b) Perform the cobalt nitrate test with the second portion of the ptt.
Pink mass.
Shows **Mg**</td><td colspan="2">Filt. Evaporate to dryness in a china dish. Again evaporate with 5 ml of conc. HCl. Heat to expel ammonium salts. Take up the residue with 5 ml of distilled water and add sodium cobaltinitrite solution.</td></tr>
<tr><td>Ppt.
yellow.
Shows **K**</td><td>(a) Heat a portion of the original mixture with sodium hydroxide solution. Ammonia gas is given off.
Shows
Ammonium Salts
(b) Perform the flame test with another portion of the original mixture. Golden-yellow persistent flame.
Shows **Na**</td></tr>
</table>

TABLE IV

(Precipitate obtained in *Procedure V*)

The precipitate may contain sulphides of Hg, Pb, Bi, Cu, Cd, Ni and Co. Boil with 1 : 2 nitric acid and filter.

<table>
<tr><td rowspan="6">Ppt. HgS. Dissolve in conc. HCl and a crystal of $KClO_3$. Add $SnCl_2$ solution. A white ppt. changing to grey. Shows **Hg**</td><td colspan="6">Filt. Nitrates of Pb, Bi, Cu, Cd, Ni and Co. Evaporate to fumes with conc. H_2SO_4. Allow to cool, dilute and filter.</td></tr>
<tr><td rowspan="5">Ppt. $PbSO_4$. Soluble in CH_3COONH_4. Add K_2CrO_4. A yellow ppt. Shows **Pb**</td><td colspan="5">Filt. Sulphates of Bi, Cu, Cd, Ni and Co. Add NH_4OH in excess and filter.</td></tr>
<tr><td rowspan="4">Ppt. white. Dissolve in dil. HCl and add sodium stannite solution. Black ppt. Shows **Bi**</td><td colspan="4">Filt. Ammonia complexes of Cu, Cd, Ni and Co. Acidify with dil. HCl, concentrate to a small volume, add $Na_2S_2O_3$ (solid), boil and filter.</td></tr>
<tr><td rowspan="3">Ppt. Black CuS. Shows **Cu**</td><td colspan="3">Filt. Chlorides of Cd, Ni and Co. Add $(NH_4)_2CO_3$ (better solid) in excess and filter.</td></tr>
<tr><td rowspan="2">Ppt. White $CdCO_3$. Charcoal Cavity test. Brown mass. Shows **Cd**</td><td colspan="2">Filt. Ammonia complexes of Ni and Co. Add acetic acid in excess and then KNO_2. Filter after 10 minutes.</td></tr>
<tr><td>Ppt. $K_3[Co(NO_2)_6]$. Test with borax bead. Blue bead. Shows **Co**</td><td>Filt. Add dimethylglyoxime and make ammoniacal. A red ppt. or coloration. Shows **Ni**</td></tr>
</table>

TABLE V

(Precipitate obtained in *Procedure VI*)

The precipitate may contain the hydroxides of manganese, iron and alkaline earths. Boil with conc. HNO_3 and $KClO_3$. Filter through glass wool.

<table>
<tr><td rowspan="2">Ppt. MnO_2.</td><td colspan="2">Filt. Nitrates of Fe and alkaline earths. Test for phosphate. If present, test for iron in a small portion by NH_4CNS test and eliminate phosphate from the remaining solution as $FePO_4$ by basic acetate method. Boil and filter hot. If phosphate is absent add NH_4OH in excess and filter.</td></tr>
<tr><td>Ppt. Hydroxide or phosphate of Fe.</td><td>Filt. Acetates of alkaline earths. Ba, Sr, Ca and Mg. Test as usual.</td></tr>
</table>

References p. 517.

TABLE VI

(Filtrate obtained in *Procedure VI*)

The solution may contain Na_2CrO_4, Na_2ZnO_2, $NaAlO_2$. Acidify with dil. HNO_3, add NH_4OH in excess and filter.

Ppt. $Al(OH)_3$. Test by cobalt nitrate test.	Filt. $(NH_4)_2CrO_4$ and $[Zn(NH_3)_6](OH)_2$. Acidify with acetic acid and add $BaCl_2$. Filter.	
Blue mass. Shows **Al**	Ppt. Yellow $BaCrO_4$. Shows **Cr**	Filt. $Zn(CH_3COO)_2$. Add $K_4[Fe(CN)_6]$ solution. A white ppt. Shows **Zn**

SUMMARY

A brief outline is given of the new scheme of qualitative analysis for common elements based upon the decomposition of thiosalts.

RÉSUMÉ

Un bref aperçu est donné au sujet du nouveau schéma d'analyse qualitative des éléments courants, basé sur la décomposition des thiosels.

ZUSAMMENFASSUNG

Ein kurzer Überblick wird über das neue Schema der qualitativen Analyse der gebräuchlichen Elemente gegeben, welches auf der Zerstörung der Thiosalze basiert.

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SOME OBSERVATIONS ON THE PRECIPITATION OF GROUP II METALS IN QUALITATIVE ANALYSIS

by

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INTRODUCTION

Group II of the classical scheme of qualitative analysis (*i.e.*, the group in which arsenic, antimony, bismuth, cadmium, copper, lead, mercury and tin are precipitated as sulphides) is the most troublesome of all the analytical groups. Some of the reasons for this are as follows:

1. Group II contains the greatest number of elements.
2. A clear-cut separation into Groups IIA and IIB is never achieved by the conventional reagents.
3. The acidity must be carefully adjusted to about $0.5N$ to avoid the incomplete precipitation, or non-precipitation, of certain sulphides. For example, the amount of cadmium remaining unprecipitated increases as the acidity rises to about $2.8N$. With the usual concentrations of qualitative analysis no precipitation occurs at all above this acidity.
4. The presence of oxidizing agents may cause the conversion of sulphide to sulphate, and bring about the precipitation of alkaline earth metals at this stage; considerable amounts of sulphur may also be produced.
5. It is necessary to convert pentavalent arsenic to the trivalent state to avoid the slow, two-stage precipitation of arsenious sulphide with concomitant deposition of sulphur.

Fairly recently, HOLNESS AND TREWICK[1] have recommended a reagent, 1% LiOH with 5% KNO_3, for separating the sulphides of Group IIA from Group IIB. A clean separation of the two groups is obtained. HOLNESS has also devised a neat and simple method for obtaining the correct acidity at which to precipitate the Group II sulphides[2]. The solution is oxidized with bromine water to convert trivalent arsenic to the pentavalent state and so avoid loss by volatilisation during the subsequent treatment[3]. It is then evaporated down to a few ml, until the constant boiling concentration of hydrochloric acid is reached (*i.e.* about $6N$), and hydrogen sulphide is then passed. After this precipitation, the hydrogen sulphide in solution is boiled out, and an equal volume of water is added, followed by a volume of $2N$ ammonia solution equal to that of the diluted solution. It will be seen that the resulting acidity is approximately $0.5N$ in hydrochloric acid, the final volume being about 25 ml. The solution is boiled and hydrogen sulphide is then passed again.

In this paper, we shall describe our attempts to overcome some of the remaining difficulties. Our investigation was confined to the macro-scale as this is still the one in general use. Presumably our final recommendations can readily be adapted to smaller scales of working.

Various methods have been proposed for the destruction of oxidizing agents, especially permanganate and dichromate. Reduction by sulphur dioxide is often mentioned in text-books, but the authors then usually go to such lengths to point out its disadvantages that only the most optimistic would be likely to use it. VOGEL recommends the use of formaldehyde or ethanol and, if pentavalent arsenic is present, reduction with ammonium iodide[4]. He does not indicate if the latter reagent can be used for all purposes. Free iodine which is produced during the reaction is removed according to the equation

$$H_2S + I_2 = 2HI + S.$$

The production of a small quantity of sulphur may not be objectionable because it can act as a carrier[5]. However, the presence of a large quantity may be inconvenient; also any colloidal sulphur produced may be oxidized to sulphate when the solution is boiled with nitric acid to remove organic acids, or to oxidize iron (II) to iron (III).

The use of ammonium iodide was investigated further, together with that of two other reagents for the destruction of the more powerful oxidants. The behaviour of these reagents with less commonly occurring ions likely to be present at this stage of the analysis was also examined, so that eventually a procedure might be obtained which could be extended to the analysis of mixtures of the rarer elements. So that reducing agents which do not reduce arsenate might be employed, conditions were established under which arsenic penta-sulphide could be precipitated conveniently with the minimum amount of reduction. Finally, a more convenient separation of the Group IIB metals was examined.

THE EXAMINATION OF REDUCING AGENTS

The following reagents were tried:

(a) a solution of hydrogen peroxide (20 vol.)
(b) a normal solution of ammonium iodide.
(c) metallic mercury.

One other obvious reducing reagent, ammonium nitrite, was not examined because it was not available commercially, presumably owing to its unpleasant characteristics. Although potassium nitrite removed permanganate and dichromate, and the excess of nitrite could be removed by boiling, the nitrate ion produced during the reduction gave colloidal sulphur when hydrogen sulphide was passed.

Reagents (a), (b) and (c) all destroyed dichromate and permanganate rapidly in acid solution, but the reactions of (b) and (c) with other ions present at this stage of the analysis introduced complications, especially when the less common elements were present. The results are summarized in the following tables. Only single reactants were treated in any one experiment.

REACTIONS WITH AMMONIUM IODIDE

1 ml of normal ammonium iodide was added to about 10 ml of a solution of the reactant in 2*N* hydrochloric acid. The solution was evaporated to constant boiling acidity, filtered if necessary and treated with hydrogen sulphide following the procedure described by HOLNESS[2].

In this way, most of the iodine released was driven off before the passage of hydrogen sulphide, and the formation of colloidal sulphur was avoided.

Element	*Reaction with NH_4I*	*Remarks*
As^{V}	Reduced to As^{III}	Loss of As^{III} by volatilisation during evaporation.
Cu^{II}	Precipitation of Cu_2I_2	
Hg^{II}	$[HgI_4]^{-2}$ formed with excess reagent.	HgS was not precipitated readily from solution.
Fe^{III}	Reduced to Fe^{II}	
Se^{IV}	Reduced to the element	
Se^{VI}	Decomposed on prolonged boiling.	
Te^{IV}	Partial precipitation of TeI_4; $[TeI_6]^{-2}$ remained in solution.	
Te^{VI}	$[TeI_6]^{-2}$produced.	
Pt^{IV}	Highly coloured solution.	$[PtI_6]^{-2}$formed.
Au^{III}	Precipitate of gold iodide, redissolving in excess reagent.	$[AuI_4]^{-}$formed.
V^{V}	Reduced to vanadyl.	

REACTIONS WITH METALLIC MERCURY

Approximately 10 ml of solutions acidified with hydrochloric acid (to 2*N*) were shaken for 5 minutes with about 2 ml of mercury. The solutions were separated off and hydrogen sulphide passed as before.

Element	*Reaction with Mercury*	*Remarks*
As^{V}	No reaction	
Cu^{II}	No reaction	
Hg^{II}	Precipitate of Hg_2Cl_2	
Fe^{III}	Reduced to Fe^{II}	
Se^{IV}	Not reduced in 2*N* HCl	Reduced in 6*N* HCl
Se^{VI}	No reaction	Reduced to Se^{IV} by boiling with HCl.
Te^{IV}	Readily reduced	
Te^{VI}	No reaction	
Pt^{IV}	Reduced to the metal.	
Au^{III}	Reduced to the metal.	
V^{V}	Reduced slowly to the vanadyl state in 2*N* HCl.	Time for complete reaction was 7 minutes.

REACTIONS WITH HYDROGEN PEROXIDE

The test solution was treated with 1-2 ml of hydrogen peroxide (20 vol.). The procedure used with ammonium iodide solutions was then followed; the boiling in this treatment served to destroy the excess peroxide.

Element	*Reaction with H_2O_2*	*Remarks*
As^{V}	No reaction	As^{III} oxidized to As^{V}
Cu^{II}	No reaction	
Hg^{II}	No reaction	
Fe^{III}	No reaction	Fe^{II} oxidized to Fe^{III}, which gave S on passing H_2S.
Se^{IV}	Some oxidation	Any Se^{VI} produced was reconverted to Se^{IV} on boiling with HCl.
Te^{IV}	Some oxidation	As for Se^{IV}.
Pt^{IV}	No reaction	Some solutions gave a very slight precipitate,
Au^{III}	No reaction	
V^{V}	Oxidized to pervanadic acid	This was readily reconverted to V^{V} on boiling with HCl.

Ammonium iodide, might be added after the evaporation in order to avoid loss of arsenic during boiling. In this case the free iodine would not be removed, and unless this were extracted, *e.g.* with chloroform, the production of sulphur would not be avoided. One disadvantage in using mercury was the inconvenience in separating the solutions from the precipitates produced and the residual mercury, before hydrogen sulphide treatment. It would also be necessary to apply a specific test for mercury (II) immediately after the Group I separation. Hydrogen peroxide appeared to be the best reagent as it gave fewest complications with other ions likely to be present. It oxidized arsenic (III) to arsenic (V) (thereby ensuring its retention in solution during evaporation), and the excess reagent was destroyed on boiling. The production of sulphur when iron or vanadium was present could not be avoided.

The formation of sulphate ion by the action of oxidizing agents on hydrogen sulphide was examined. The ion investigated was treated with hydrogen sulphide in hot 6*N* hydrochloric acid, and the HOLNESS procedure was followed. The solution was filtered, and the filtrate boiled free from hydrogen sulphide and cooled. It was tested for sulphate with barium chloride solution.

Ion	*Reaction*
MnO_4^{-2}	SO_4^{-2} produced
$Cr_2O_7^{-2}$	SO_4^{-2} produced
VO_3^-	No SO_4^{-2} produced
Fe^{+3}	No SO_4^{-2} produced
H_2O_2	No SO_4^{-2} produced when a solution $2N$ to HCl was evaporated to constant boiling acid before passing H_2S. If the excess H_2O_2 was not destroyed, large quantities of SO_4^{-2} resulted.

Thus, in conjunction with the HOLNESS procedure for the precipitation of Group II, hydrogen peroxide could be used to destroy dichromate and permanganate, but it remained to find a convenient means of precipitating arsenic pentasulphide.

THE PRECIPITATION OF ARSENIC PENTASULPHIDE

According to IBBOTSON AND AITCHISON[6], who quote the results of numerous investigators, arsenic sulphide is precipitated quantitatively from solutions $6N$ in hydrochloric acid at a temperature of 70° C. The precipitate can be weighed as As_2S_5. From the standpoint of qualitative analysis it would be of little consequence if such a precipitate contained a small amount of arsenious sulphide; and, provided that the optimum conditions for precipitation were not too exacting, the direct precipitation of As_2S_5 would be a simple means of eliminating the pre-reduction of arsenite.

Solutions of M sodium arsenate (50 ml) were diluted with sufficient concentrated hydrochloric acid to bring them to the desired acidity. Hydrogen sulphide was then introduced using the "pressure-absorption" method in a 250 ml flask. Four series of experiments were carried out.

1. *Precipitation from solutions 3N to 7.8N in hydrochloric acid at room temperature.* Precipitation was incomplete in 30 minutes or less, and in one case (5.2N HCl) in 20 hours.
2. *Precipitation from boiling solutions 5.2 N and 7.2N in hydrochloric acid.* The solutions were boiled and hydrogen sulphide was passed as they cooled between 105° and 85°. Some precipitations were complete, but not all, in twenty minutes.
3. *Precipitation at 70° from solutions 6N in hydrochloric acid, during 20 minutes.* Various methods of passing hydrogen sulphide were tried, and the "pressure-absorption" method was found the most convenient. In 20 minutes precipitation was always complete, and the precipitates easy to handle.
4. *Precipitation at 70° from solutions 6N in hydrochloric acid, varying the time for the reaction.* The time was varied from 20 minutes to 3 minutes. Complete precipitation took at least 8 minutes using these volumes of solution (*i.e.* about 100 ml).

In all cases the precipitates were filtered off, washed with hydrogen sulphide water, and sucked dry at the pump. Finally they were dried on a vacuum hot plate at 40° for an hour. The dried precipitates were each extracted with carbon disulphide in a Soxhlet extractor for 1½ hours. The results indicated that solutions precipitated at 70° at an acidity $6N$ to hydrochloric acid yielded much less sulphur than those precipitated under the other conditions and there was rarely more than 10% reduction of As (V).

It so happens that the HOLNESS procedure for the adjustment of the acidity provides these conditions, hence this can still be applied with only slight modification.

A series of experiments was made reproducing the conditions of qualitative analysis more closely. Quantities of sodium arsenite similar to those found in quali-

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tative analysis were dissolved in 20 ml of 2*N* hydrochloric acid. The solutions were treated with 2 ml of hydrogen peroxide (20 vol.) and evaporated down to a volume of about 5 ml. Hydrogen sulphide was passed into the solution while its temperature was maintained at as near 70° as possible. It was found that complete precipitation took at least 8 minutes, and the precipitates contained rather more sulphur than did those formed from larger volumes of solution. In the full qualitative procedure, however, it was possible to reduce the time of this precipitation to 5 minutes, and any remaining arsenic precipitated with the other Group II sulphides.

In these experiments, it was important to release the pressure of gas over the solution from time to time, and flush the apparatus out, especially in the early stages of precipitation. A small conical flask was used, with the delivery tube arranged so that the solution could be flushed whilst the flask was heated on a waterbath.

THE SEPARATION OF GROUP IIB ELEMENTS

IBBOTSON AND AITCHISON[7] have quoted the work of several investigators who established the optimum acidities at which arsenic, antimony and tin could be precipitated individually. As these ranges are sufficiently far apart it seemed likely that the separation of all three should be possible.

Tests were carried out to determine the upper limits of acidity for the precipitation of antimony (6.5*N* hydrochloric acid), stannic tin (3*N* hydrochloric acid) and stannous tin (about 2*N* in hydrochloric acid), at room temperature. It was shown that complete precipitation of the sulphides could be obtained at the following acidities: —

As_2S_5, As_2S_3	7*N* HCl at 70° in 8 minutes.
Sb_2S_3	5*N* HCl at room temperature.
Sn^{IV}	2*N* HCl at room temperature.
Sn^{II}	0.5*N*-0.3*N* at room temperature.

Mixtures of arsenic (tri- and penta- valent), antimony and tin were then separated by successive passages of hydrogen sulphide followed by filtration and dilution. (It was not possible to separate the two forms of tin by precipitation from solutions of controlled acidity). The problem remained to establish the initial acidity of the solution of these elements, or of their sulphides, for precipitation. Following HOLNESS AND TREWICK[2], the sulphides obtained in the Group precipitation were dissolved in a reagent containing 1% lithium hydroxide with 5% potassium nitrate. This reagent is *N*/4 in alkali. The hot lithium hydroxide solution was therefore poured into twice its volume of concentrated (11*N*) hydrochloric acid, giving a solution approximately 7*N* in hydrochloric acid. Only yellow arsenic sulphides were precipitated. The filtrate was cooled and diluted with an equal volume of water, giving a solution about 3.5*N* to hydrochloric acid, when antimony sulphide was deposited. To the filtrate was added an equal volume of 2*N* ammonium hydroxide giving an acidity approximately 0.5*N* to hydrochloric acid for the precipitation of yellow stannic tin. It was necessary to pass a little hydrogen sulphide at each precipitation.

The reverse procedure, *i.e.* that of adding the concentrated acid to the lithium hydroxide solution, gave an initial precipitate of Sb_2S_3 that did not entirely redissolve as the acidity mounted.

Successive extraction of the sulphides (precipitated from the lithium hydroxide extract) using hydrochloric acid of appropriate concentrations, was also tried. The results were satisfactory, but it was considered preferable to precipitate from solutions of controlled acidity because the precipitated sulphides would contain varying amounts of moisture which might affect the final acid concentrations.

Recommended procedure

The following procedure is recommended after Group I of the analysis has been removed: —

To the filtrate is added 2 ml of 20 vol. hydrogen peroxide, the solution is warmed, and then evaporated down carefully to 4 or 5 ml. One drop of concentrated hydrochloric acid is added, the solution is boiled and hydrogen sulphide is passed preferably in a small conical flask with occasional flushing. Treatment with hydrogen sulphide is continued for 5 to 6 minutes while the temperature of the flask and its contents is maintained near 70° C.

Any precipitate formed is allowed to remain in the solution while hydrogen sulphide is boiled out, and an equal volume of water is added, followed by a volume of $2N$ ammonium hydroxide equal to that of the diluted solution. The solution is heated to boiling and hydrogen sulphide is passed as it cools.

The sulphide precipitate is heated just to boiling with 1% lithium hydroxide — 5% potassium nitrate reagent in the normal way, and the resulting hot solution is poured into twice its volume of concentrated hydrochloric acid. A little hydrogen sulphide is passed, and the yellow arsenic sulphide is removed. The filtrate is cooled, diluted with an equal volume of water, hydrogen sulphide is passed and orange antimony sulphide is filtered off. The remaining solution is treated with an equal volume of $2N$ ammonium hydroxide, hydrogen sulphide is passed, when yellow SnS_2 is precipitated.

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SUMMARY

Difficulties in the precipitation of Group II of the classical scheme of qualitative inorganic analysis are discussed. Three reagents for the destruction of permanganate and dichromate have been examined; hydrogen peroxide was found to be most suitable. Conditions have been established whereby As_2S_5 can be precipitated, thus avoiding the necessity for reducing As^V before passing hydrogen sulphide. A simple separation of the Group IIB elements, based on the stepwise precipitation of their sulphides from solutions of controlled acidity, is proposed.

These modifications have been adapted to the procedures of HOLNESS[2] and HOLNESS AND TREWICK[1], for adjusting the acidity and for dividing the sulphide precipitates into the two sub-groups.

RÉSUMÉ

Les difficultés rencontrées lors de la précipitation des éléments du groupe II par la méthode classique de l'analyse inorganique qualitative sont examinées. Trois réactifs de destruction du permanganate et du dichromate sont étudiés; le peroxyde d'hydrogène semble être le plus avantageux. Des conditions ont été déterminées pour précipiter As_2S_5 afin d'éviter la réduction de As^V avant le passage de l'hydrogène sulfuré. Une méthode simple est proposée pour séparer les éléments du groupe IIB, par précipitation fractionnée de leurs sulfures à pH contrôlé. Ces modifications ont été adaptées aux procédés de HOLNESS[2] et de HOLNESS ET TREWICK[1] pour ajustement de l'acidité et pour le partage des précipités de sulfures en deux sous-groupes.

ZUSAMMENFASSUNG

Die während der Ausfällung der Elemente der Gruppe II mittels der klassischen Methode der anorganischen qualitativen Analyse, auftretenden Schwierigkeiten wurden untersucht. Es wurden drei Reagenzien zur Zerstörung des Permanganates und des Bichromates geprüft. Wasserstoff-

peroxyd scheint das vorteilhafteste zu sein. Die Bedingungen wurden bestimmt, um As_2O_5 auszufällen und somit die Reduktion des As^V vor der Durchleitung von Schwefelwasserstoff zu vermeiden. Es wird eine einfache Methode vorgeschlagen, um die Elemente der Gruppe IIB abzutrennen mittels einer fraktionierten Ausfällung ihrer Sulfide bei kontrolliertem pH. Diese Modifikationen wurden auf die Verfahren von Holness[2] und Holness und Trewick[1] um die geeignete Acidität zu erreichen und zur Aufteilung der Sulfid-Niederschläge in zwei Untergruppen angewendet.

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ANALYTISCHE VERWERTUNGEN DER DEMASKIERUNG VON FERROCYANID

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Die grosse Stabilität von Ferro- und Ferricyanidionen zeigt sich in der Fällbarkeit vieler Schwermetallferro- und ferricyanide aus neutraler oder saurer Lösung, in der Isolierbarkeit von Ferro- und Ferricyanwasserstoffsäure und an dem Ausbleiben (Maskierung) von für Fe^{+2}, Fe^{+3} und CN^--Ionen charakteristischen Reaktionen. Obwohl demnach die Gleichgewichte

$$[Fe(CN)_6]^{-4} \rightleftharpoons Fe^{+2} + 6\ CN^-$$

und

$$[Fe(CN)_6]^{-3} \rightleftharpoons Fe^{+3} + 6\ CN^-$$

weitgehend auf der Seite der komplexen Anionen liegen, so müssen deren Dissoziationsprodukte zu minimalen Beträgen vorhanden und durch geeignete Partner den Gleichgewichten entziehbar sein. Es durfte erwartet werden, dass die gleichzeitige Einwirkung von Reagenzien auf Fe^{+2}, Fe^{+3} und CN^--Ionen besonders effektvoll sein und zu einer Demaskierung der Bestandteile der komplexen Anionen führen müsse. Dies ist tatsächlich der Fall, wie die nachstehenden, auch für Vorlesungszwecke geeigneten Versuche sehr anschaulich zeigen:

1. 4 ml einer 5%-igen Kaliumferrocyanidlösung werden mit 1 ml Salzsäure (1 : 1) versetzt und die Lösung auf zwei Eprouvetten verteilt. Zu einer Eprouvette wird ein Tropfen 0.5*N* Sublimat zugesetzt. Nach etwa 3 Minuten beginnt die quecksilberhaltige Lösung eine blaue Farbe anzunehmen, während die quecksilberfreie Lösung unverändert bleibt. Dieser Effekt tritt schneller ein, wenn die beiden Eprouvetten in auf 60° erwärmtes Wasser eingetaucht werden.

   In der quecksilberhaltigen Lösung, erfolgt durch Bildung von löslichem undissozierten Quecksilbercyanid eine Demaskierung von Fe^{+2}-Ionen gemäss

   $$[Fe(CN)_6]^{-4} + 3Hg^{+2} \rightarrow 3[Hg(CN)_6]^{-4} + Fe^{+2}$$

   Die freigelegten Ferroionen bilden mit überschüssigem Ferrocyanid zunächst weisses Ferro-Ferrocyanid $Fe_2[Fe(CN)_6]$ das an der Luft in Berlinerblau übergeht.

2. In zwei Eprouvetten werden je 2 ml einer 5%-ig essigsauren Lösung von Kaliumferricyanid, die einige Tropfen alkoholische 8-Hydroxychinolinlösung enthält, gebracht. Zu einer der Lösungen wird ein Tropfen 0.5*N* Sublimat gebracht und beide Eprouvetten in siedendes Wasser getaucht. In der quecksilberhaltigen Lösung entsteht ein blaugrüner Niederschlag von Eisen(III) Oxinat, während die quecksilberfreie Lösung unverändert bleibt.

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In der quecksilberhaltigen Lösung erfolgt, analog wie bei 1., zunächst Demaskierung gemäss

$$[Fe(CN)_6]^{-3} + 3Hg^{+2} \rightarrow 3Hg(CN)_2 + Fe^{+3}$$

Die freigelegten Ferriionen reagieren mit Oxin unter Bildung von unlöslichem blaugrünen Eisen(III) Oxinat.

$$Fe^{+3} + 3HOx \rightarrow Fe(Ox)_3 + 3H^+$$

3. Zu 2 ml einer 5%-igen Kaliumferrocyanidlösung wird 1 ml einer ammoniakalischen Silberoxydlösung gebracht (2 ml 2%-ig $AgNO_3$-Lösung mit NaOH versetzt und gebildetes Ag_2O durch Zusatz von verdünntem Ammoniak gelöst) und erwärmt. Es entsteht ein braunschwarzer Niederschlag. Dieser Effekt (silberfreie alkalische Ferrocyanidlösung bleibt unverändert) ist folgendermassen zu erklären: Es erfolgt zunächst Demaskierung gemäss

$$[Fe(CN)_6]^{-4} + 6Ag^+ \rightarrow 6AgCN + Fe^{+2}$$

Die freigelegten Ferroionen reagieren mit überschüssigen Ag^+- und OH^--Ionen gemäss

$$Fe^{+2} + Ag^+ + 3OH^- \rightarrow Fe(OH)_3 + Ag^\circ$$

4. Ein analoger Versuch wie 2. wird mit einer 5%-igen Kaliumferricyanidlösung ausgeführt. Es kommt zur Bildung von braunem Eisen(III) Hydroxyd gemäss

$$[Fe(CN)_6]^{-3} + 6Ag^+ \rightarrow 6AgCN + Fe^{+3}$$

$$Fe^{+3} + 3OH^- \rightarrow Fe(OH)_3$$

Die Versuche 1-4 zeigen, dass eine Demaskierung des Eisens in Alkaliferro- und Ferricyanid sowohl in saurer als auch in alkalischer Lösung möglich ist; es war deshalb naheliegend zu versuchen, diese Demaskierung analytisch zu verwerten.

Da wir für den empfindlichen Nachweis von Ferroionen im *αα'* Dipyridyl ein in saurer, neutraler und alkalischer Lösung wirksames Reagens besitzen[1], wurde das Verhalten einer ammoniakalischen, dipyridylhaltigen Kaliumferrocyanidlösung gegenüber Ag-, Hg-, und Pd-Ionen geprüft, die im Einklang mit der Säureresistenz der Cyanide ein besonders starkes Bindevermögen für Cyan besitzen. Es hat sich gezeigt, dass der von diesen Jonen bewirkte Demaskierungseffekt so stark ist, dass durch die Bildung von roten $[Fe(\alpha\alpha'dip)_3]^{+2}$-Ionen zu einem spezifischen Nachweis von Ferrocyanid, sowie zu selektiven Nachweisen von Silber, Quecksilber und Palladium gelangt werden kann. Sämtliche Nachweise sind so empfindlich, dass sie als Tropfenreaktionen ausgeführt werden können.

An Stelle von *αα'* Dipyridyl kann natürlich auch das analog reagierende und als Eisenreagens sogar empfindlichere *αα'* Phenanthrolin[2] verwendet werden. Wird die Demaskierung in pyridinhaltiger Lösung vorgenommen, so können freigelegte Ferroionen auch mit Dimethylglyoxim durch eine Orangefärbung nachgewiesen werden[3] (Bildung von löslichen Pyridinsalzen der Eisen(II)dimethylglyoximsäure)[4]. Die Empfindlichkeit dieses Nachweises ist allerdings geringer als die der Farbreaktionen mit *αα'* Dipyridyl oder *αα'* Phenanthrolin.

I. NACHWEIS VON FERROCYANIDEN

Die besten Bedingungen für die Realisierung der Demaskierung und der Eisen(II) Dipyridylreaktion bestehen bei Erwärmung der Probelösung mit wasserunlöslichem

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Mercuriamidochlorid. Als Bruttogleichung der Demaskierung darf angenommen werden:

$$[Fe(CN)_6]^{-4} + 3HgNH_2^+ + H_2O \rightarrow Fe^{+2} + 3Hg(CN)_2 + 3NH_3 + 3OH^-$$

oder

$$[Fe(CN)_6]^{-4} + 3HgNH_2Cl + 3H_2O \rightarrow Fe^{+2} + 3Hg(CN)_2 + 3NH_3 + 3OH^- + 3Cl^-$$

Für die obigen Umsetzungen, an die sich noch die Bildung von $[Hg(CN)_4]^{-2}$-ionen anschliesst (vgl. II) spricht, dass die farblose Suspension von $HgNH_2Cl$ in einer phenolphtaleinhaltigen Kaliumferrocyanidlösung bei Erwärmung rot wird.

Die Verwendung von festem Mercuriamidochlorid als Demaskierungensreagens hat nicht nur den Vorteil, dass beim Nachweis keine empfindlichkeitsvermindernde Volumszunahme erfolgt, sondern, dass auch saure Lösungen geprüft werden können, weil durch die Reaktion

$$HgNH_2Cl + 2H^+ \rightarrow Hg^{+2} + NH_4^+ + Cl^-$$

Neutralisation erfolgt[5].

Arbeitsweise: In einer Mikroeprouvette wird ein Tropfen der sauren, neutralen oder sodaalkalischen Probelösung mit einem Tropfen alkoholischer Dipyridyllösung und einigen mg Mercuriamidochlorid versetzt und im Wasserbad erwärmt. Je nach der Menge Ferrocyanid entsteht eine mehr oder weniger intensive Rotfärbung. Bei Vorliegen von sauren Lösungen ist nach Zusatz von $HgNH_2Cl$ einige Minuten zu warten und erst dann zu erwärmen.

Erfassungsgrenze: 0.2 γ Kaliumferrocyanid
Grenzverdünnung: 1:250,000

Reagenzien:
1. 1%-ig alkoholische Lösung von *αα'* Dipyridyl
2. Mercuriamidochlorid (fest)

Die obige Erfassungsgrenze wird noch erreicht in Gegenwart von 1000 γ Kaliumferricyanid.

II. NACHWEIS VON QUECKSILBER, SILBER UND PALLADIUM

Eine ammoniakalischen Lösung von Kaliumferrocyanid bleibt lediglich nach Zusatz von Palladiumionen klar; mit Quecksilber- und Silberionen entstehen Niederschläge von $HgNH_2Cl$ bzw. $Ag_4[Fe(CN)_6]$. In allen drei Fällen werden bei Erwärmung in Gegenwart von *αα'* Dipyridyl durch die freigelegten Ferroionen rote $[Fe(\alpha\alpha'dip)_3]^{+2}$-Ionen gebildet. Da beim Nachweis stets Kaliumferrocyanid im Überschuss verwendet wird, so ist anzunehmen, dass primär gebildetes Quecksilber (Ag und Pd)-cyanid auf Ferrocyanid einwirkt unter Bildung von löslichen komplexen Metallcyanionen, z.B.

$$[Fe(CN)_6]^{-4} + 3Hg(CN)_2 \rightarrow 3[Hg(CN)_4]^{-2} + Fe^{+2}$$

Dass obige Reaktion tatsächlich erfolgt, zeigt sich daran, dass eine ammoniakalische dipyridylhaltige Kaliumferrocyanidlösung bei Erwärmung mit wasserlöslichem Quecksilbercyanid rot wird. Der gleiche Effekt wird durch wasserunlösliches Palladium- und Silbercyanid erzielt.

Arbeitsweise: In einer Mikroeprouvette wird zu einem Tropfen Kaliumferricyanidlösung je ein Tropfen Ammoniak und alkoholische *αα'* Dipyridyllösung gebracht. Zu dieser Mischung wird ein

Literatur S. 530.

Tropfen der Probelösung zugegeben und im Wasserbad erwärmt. Je nach der Menge an Metall entsteht eine mehr oder weniger intensive Rotfärbung.

Erfassungsgrenzen: 0.5 γ Quecksilber (1:100,000)
2 ,, Silber (1:25,000)
2 ,, Palladium (1:25,000)

Das hier beschriebene Verfahren ist von beschränkter Anwendbarkeit, weil es in ammoniakalischer Lösung auszuführen ist und demnach Abwesenheit oder vorherige Abtrennung von durch Ammoniak fällbaren Metallsalzen erfordert.

Von erheblichem Interesse dürfte obige Maskierungsreaktion für den schnellen Nachweis von Quecksilber in pharmazeutischen Präparaten sein. Wir haben eine Reihe von einschlägigen Präparaten untersucht, die, in fester Form (mg Mengen) der Reagenslösung zugesetzt, nach gelinder Erwärmung, häufig sogar bei Raumtemperatur durchwegs eine intensive Rotfärbung hervorriefen.

Reagenzien:
1. 1%-ige Kaliumferrocyanidlösung
2. 1%-ig alkoholische Lösung von *αα'* Dipyridyl
3. 2*N* Ammoniak

III. NACHWEIS VON SILBERHALIDEN

Die der Demaskierung von Eisen(II) aus Alkaliferrocyanidlösungen zugrundeliegende Umsetzung ist

$$[Fe(CN)_6]^{-4} + 3AgHal \rightarrow 3\ [Ag(CN)_2]^- + 3Hal^- + Fe^{+2}$$

In ammoniakalischem Milieu sind bei in Ammoniak löslichen Silberhaliden die dabei gebildeten $[Ag(NH_3)_2]^+$-Ionen wirksam. Bemerkenswert ist die Reaktionsfähigkeit von in Ammoniak völlig unlöslichem Silberjodid und Silberferrocyanid. Sie steht in Übereinstimmung mit der Löslichkeit dieser Verbindungen in überschüssigem Kaliumcyanid unter Bildung von $[Ag(CN)_2]^-$-Ionen.

Arbeitsweise: In einer Mikroeprouvette wird eine minimale Menge Silberhalid mit je einem Tropfen Ammoniak, Kaliumferrocyanid und *αα'* Dipyridyllösung versetzt und im Wasserbad erwärmt. Je nach der Menge Silberhalid entsteht nach einigen Minuten eine mehr oder weniger intensive Rotfärbung.

Reagenzien: Wie unter II angeführt.

Das Verfahren wurde überprüft an: AgCl, AgBr, AgJ, AgCN, AgCNS, $Ag_4[Fe(CN)_6]$, $Ag_3[Fe(CN)_6]$ und $Ag_3[Co(CN)_6]$.

Wir danken an dieser Stelle dem Conselho Nacional de Pesquisas für die uns gewährte Förderung.

ZUSAMMENFASSUNG

Kaliumferro- und Kaliumferricyanid sind in saurer, neutraler und alkalischer Lösung durch Metallionen demaskierbar, die säurebeständige Cyanide bilden.

Eine ammoniakalische Kaliumferrocyanidlösung, die *αα'* Dipyridyl oder *αα'* Phenanthrolin enthält, wird bei Demaskierung rot infolge Bildung von komplexen Kationen des zweiwertigen Eisens mit *αα'* Dipyridyl bzw. *αα'* Phenanthrolin.

Es werden Nachweise von Ferrocyanid, Quecksilber, Silber, Palladium und Silberhaliden beschrieben, die auf der erwähnten Demaskierung beruhen und in Form von Tüpfelreaktionen ausführbar sind.

Das Verfahren ist besonders empfehlenswert zum Nachweis von Quecksilber in pharmazeutischen Präparaten.

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SUMMARY

Potassium ferrocyanide and ferricyanide can be decomposed in acid, neutral and alkaline solution by metal ions, which form acid-resisting cyanides.

An ammoniacal potassium ferrocyanide solution, containing *αα'*-dipyridyl or *αα'*-phenanthroline, becomes red when demasked, owing to formation of complex cations of bivalent iron with *αα'*-dipyridyl or *αα'*-phenanthroline.

A description is given of the detection of ferrocyanide, mercury, silver, palladium and silver halides, which depends on this demasking and can be carried out in the form of spot tests.

The procedure described is especially useful for the detection of mercury in pharmaceutical preparations.

RÉSUMÉ

Les ferro- et ferricyanures de potassium peuvent être décomposés en solutions acides, neutres et alcalines par des ions métalliques, capables de former des cyanures stables vis-à-vis des acides.

Une solution ammoniacale de ferrocyanure de potassium, renfermant de l'*α-α'*dipyridyle ou de l'*α-α'* phénanthroline deviendra rouge après ,,démasquage'', par formation des complexes de l'*α-α'* dipyridyle ou de l'*α-α'* phénanthroline avec le fer(II).

On décrit les indentifications des: ferrocyanure, mercure, argent, palladium et halogénures d'argent, basées sur ce ,,démasquage'' et pouvant être appliquées à la technique de l'analyse à la touche.

Le procédé décrit convient spécialement à l'identification du mercure dans les produits pharmaceutiques.

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SIMPLE INSTRUMENT FOR TITRIMETRY WITHOUT VISUAL INDICATORS. GASOMETRIC TITRATIONS

X. CERIMETRY, CHLOROMETRY, NITRATE, NITRITE, HYDROXIDE AND CARBONATE DETERMINATION

by

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In previous papers[1] a gas pressure technique to locate the end-point in volumetric analysis was developed. The outstanding feature of this technique is the fact that solutions which for some reason cannot be titrated to a visual end-point, can be titrated, frequently by standard methods, in a simple, inexpensive instrument.

In the present communication a method is described, by which the titrimetric problems previously mentioned can be solved graphically. This is achieved by adding the titrant to the sample solution in measured increments and recording the corresponding gas pressure or volume of the system. The pressure or volume is then plotted against the volume of added titrant. By determining three or four points before the equivalence point and two or three after it, the end-point is found graphically at the intersection of two straight lines. Such gasometric titrations are not only much less tedious and easier to perform than the previously described drop by drop titrations, but they are also less time-consuming.

The previously described instrument can be easily adapted for use in gasometric titrations, by connecting its capillary end to a manometer or to a volume-measuring device. In the present paper only the latter combination will be described (Fig. 1), because it needs no special equipment and only elementary operating skill.

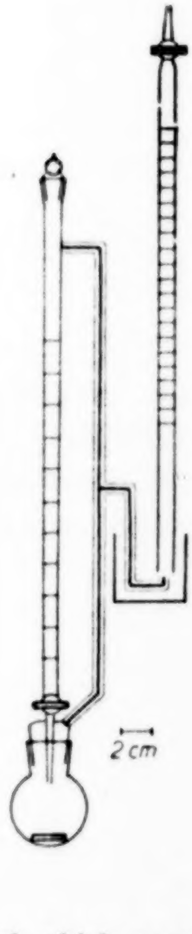

Fig. 1. The instrument.

DESCRIPTION OF INSTRUMENT

The titration vessel is a 50 ml flask, provided with a hollow glass stopper, through which passes the tip of a 10 ml buret and a capillary tube, which connects the flask and the top of the buret. The upper end of the buret is closed by a hollow glass stopper with a small hole in its side corresponding to a hole of the same size on the wall of the buret. By a slight rotatory movement of the stopper, one can make the two holes coincide or not, in order to open or close the apparatus. The capillary tube is connected with a U-tube, the short outer arm of which reaches partly into the mouth of an inverted buret which is filled with water and its lower extremity is covered by water contained in a beaker. The bore of the capillary should be 1 mm or less. The buret should have a capacity of 20 ml for titrations involving 0.1 N solutions. A magnetic stirrer provides the necessary stirring of the sample solution.

CERIMETRY

Compounds of tetrapositive cerium are very useful volumetric oxidizing agents. If the particular redox reaction liberates a gas rapidly and quantitatively, direct titration with ceric solution is possible by the gas pressure end-point technique. If the reaction is not accompanied by gas evolution, an excess of standard ceric solution is added to the sample and back-titrated with standard hydrazine sulfate or sodium azide solutions:

$$2Ce^{+4} + 2N_2H_4 \rightarrow N_2 + 2NH_4^+ + 2Ce^{+3} \quad (1)$$

$$2Ce^{+4} + 2NaN_3 \rightarrow 3N_2 + 2Na^+ + 2Ce^{+3} \quad (2)$$

Ceric ions were titrated with azide solution by the gas pressure end-point technique previously described[1]. Results are given in the first part of Table I.

TABLE I

TITRATION OF CERIC NITRATE SOLUTION WITH SODIUM AZIDE SOLUTION

ml 0.1000N Ce^{+4} taken		*ml approx. 0.1N NaN_3 consumed*		
		Drop by drop gas pressure end-point	Color end-point	Δ%
5.00		4.28		
5.00		4.28		
5.00		4.26		
	mean	4.27	mean 4.28	−0.23
	Procedure	I		
5.00		4.27		
5.00		4.28		
5.00		4.25		
	mean	4.27	mean 4.28	−0.23

The graphical procedure, as outlined below, was used to find the values in the second part of Table I. The graphs are of the type shown in Fig. 2. The intersection of the lines corresponding to the reaction (gas evolution) and to excess of titrant (no gas evolution) marks the end-point.

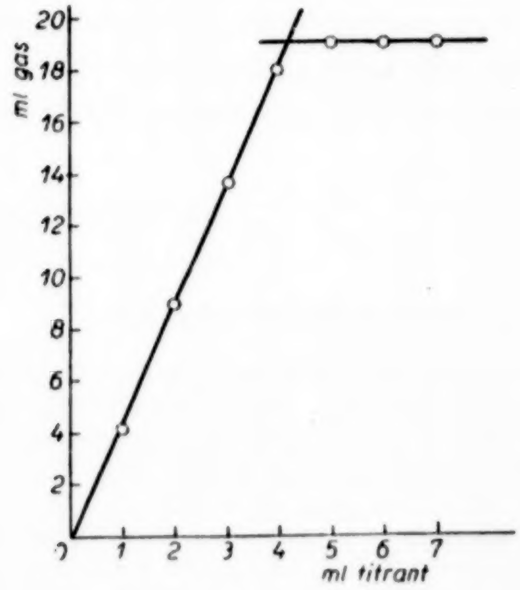

Fig. 2. Gasometric titration of 5.00 ml 0.1000*N* $[Ce(NO_3)_6](NH_4)_2$ solution with NaN_3 solution. End-point 4.26 ml (color end-point 4.28 ml).

Reagents

Ceric ammonium nitrate, 0.1000*N* solution in 0.5*M* sulfuric acid.

Sodium azide, approx. 0.1*N* solution. This solution can be standardized against solutions of ceric salts of known concentration. It is sufficiently stable and possesses great selectivity in its reaction with oxidizing agents.

Procedure 1

Fill the buret with water and put it in its inverted position above the extremity of the capillary tube. Open the stopcock of the buret cautiously until air has displaced the water from its upper, ungraduated part.

Transfer 5.00 to 10.00 ml of the sample solution, which contains ceric ions, to the titration flask and connect the latter with the buret containing the titrant. Put the magnetic stirrer in motion and close the stopper at the top of the buret. Add a certain volume of titrant to the flask (*e.g.* 1 ml) taking care to leave no droplet suspended from the buret tip. Read this volume exactly. At fixed intervals (*e.g.* 2 minutes) after the addition of the titrant, read the volume of water displaced from the inverted buret and immediately afterwards add another increment of titrant *etc.*. Three or four additions of titrant before the end-point and two or three afterwards are sufficient. Plot the volume of titrant against the volume of water displaced. Extend the straight-line portions of the curve to intersect. The intersection marks the end-point.

A direct gasometric titration procedure can be applied, if the ion to be determined reacts at a more rapid rate with tetrapositive cerium than another ion, whose reaction with the titrant is accompanied by gas evolution. Such a case is exemplified by the pair ferrous ion (sample)-hydrazine (indicator) in Table II.

TABLE II

TITRATION OF FERROUS AMMONIUM SULFATE SOLUTION WITH CERIC AMMONIUM NITRATE SOLUTION

ml Fe^{+2} *taken*	*ml* 0.1*N* Ce^{+4} *consumed*			
		Procedure 2	Color end-point	Δ%
5.00		5.38		
5.00		5.44		
	mean	5.41	5.38	+0.56

The graphs are of the type shown in Fig. 3.

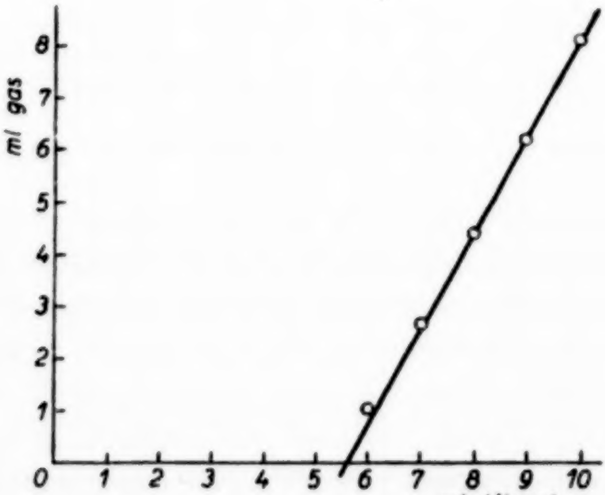

Fig. 3. Gasometric titration of 5.00 ml NaOH solution with 0.1000*N* HCl solution. End-point 5.58 ml (indicator phenolphthalein 5.58 ml).

The straight-line portion of the titration curve (gas evolution due to reaction 1) is extended to intersect the abscissa. The intersection of the two lines marks the end-point of the reaction of ferrous with ceric ion. Other cerimetric determinations of this type which can be made with reasonable accuracy include titrations of arsenite (sample)- sodium azide (indicator), arsenite (sample)- hydrazine (indicator) and ferrocyanide (sample)- hydrazine (indicator).

Reagents

Ceric ammonium nitrate, 0.1*N* solution in 0.5*M* sulfuric acid.
Hydrazine sulfate, approx. 0.1*M* solution.
Ferrous ammonium sulfate solution, acidified with sulfuric acid.

Procedure 2

Transfer 5.00 to 10.00 ml of the acid ferrous solution to the titration flask and add about 5 ml of hydrazine sulfate solution. Titrate with standard ceric solution, following the general instructions given in *Procedure* 1. The determination of three or four points during the gas evolution reaction is sufficient to locate the end-point.

CHLOROMETRY

Hypobromite can be used for oxidations not easily achieved by other means, hence the importance of a number of papers[2,3,4] showing that hypochlorite solutions are very stable when properly prepared and stored. Titrations with hypochlorite solution are usually performed in presence of excess bromide[2]:

$$ClO^- + Br^- \rightarrow BrO^- + Cl^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Thus the less stable hypobromite ion is produced and consumed in *statu nascendi*.

If the volumetric reaction of the hypobromite with the ion to be determined liberates a gas rapidly and quantitatively, direct titration of the sample solution to the gas pressure end-point is possible.

If the reaction of hypochlorite with the ion to be determined is not accompanied by gas evolution, or if an excess of this reagent has to be used, a known amount of standard hypochlorite solution is added to the sample, the excess destroyed by addition of a known amount of hydrazine sulfate or, in case the sample solution contains other ions capable of reaction with hydrazine, ammonium sulfate solution, and the excess of the latter titrated with standard hypochlorite in presence of bromide until gas evolution ceases:

$$2BrO^- + N_2H_4 \rightarrow N_2 + 2Br^- + 2H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$3BrO^- + 2NH_4^+ \rightarrow N_2 + 3Br^- + 3H_2O + 2H^+ \quad . \quad . \quad . \quad (5)$$

The oxidation of ammonium salts by hypobromites is of great practical importance, because it provides a possibility of eliminating the distillation step in the Kjeldahl determination of nitrogen. This is usually done by adding an excess of hypobromite to the neutralized digest and determining the excess with potassium iodide and thiosulfate. Direct titration of ammonium salt solutions with hypochlorite, although convenient, is not generally used, because the reaction is not very rapid and side reactions are more apt to occur in presence of excess ammonium ion. In spite of this, satisfactory, but not highly accurate, results have been reported also with direct titration methods[5,6].

TABLE III

TITRATION OF AMMONIUM SULFATE SOLUTION WITH CALCIUM HYPOCHLORITE SOLUTION

ml 0.1000M $(NH_4)_2SO_4$ *taken*	*ml 0.1304M* $Ca(ClO)_2$ *Consumed*	*Theoretical*	Δ%
Drop by drop gas pressure end-point			
5.00	11.58		
5.00	11.69		
5.00	11.62		
5.00	11.64		
5.00	11.58		
5.00	11.59		
mean	11.62	11.50	+1.04
Procedure 3			
2.50	5.73		
2.50	5.67		
2.50	5.62		
2.50	5.76		
mean	5.70	5.75	−0.87

In Table III are shown results obtained in the titration of ammonium sulfate solution by the gas pressure end-point technique of our previous papers and the graphical method. The graphs obtained are of the type shown in Fig. 2.

TABLE IV

TITRATION OF HYDRAZINE SULFATE SOLUTION WITH CALCIUM HYPOCHLORITE SOLUTION

ml 0.1000M $N_2H_4 \cdot H_2SO_4$ *taken*	*ml 0.1304M* $Ca(ClO)_2$ *Consumed*	*Theoretical*	Δ%
Drop by drop gas pressure end-point			
5.00	7.65		
5.00	7.67		
5.00	7.66		
5.00	7.64		
5.00	7.68		
5.00	7.66		
mean	7.66	7.67	−0.13
Procedure 3			
5.00	7.70		
5.00	7.72		
5.00	7.66		
mean	7.69	7.67	+0.26

Table IV shows results obtained in the titration of hydrazine sulfate solution by the same procedures. Again the graphs are shown in Figure 2.

Reagents

Calcium hypochlorite, 0.1304*M* solution. This solution was standardized against an arsenious oxide solution[7].
Sodium hydrogen phosphate, concentrated solution neutral to phenolphthalein.
Potassium bromide, solid.
Ammonium sulfate, 0.1000*M* solution.
Hydrazine sulfate, 0.1000*M* solution.

References p. 542.

Procedure 3

Transfer 5.00 to 10.00 ml of the neutral sample solution, which contains ammonium ions or hydrazine, to the titration flask, add 2 ml of the buffer solution and some potassium bromide. Titrate with standard calcium hypochlorite solution, following the general instructions outlined in *Procedure* 1.

A direct gasometric titration procedure can be applied, if the ion to be determined reacts at a more rapid rate with hypobromite than another ion, whose reaction with the titrant is accompanied by gas evolution. Such is the case with the pair arsenite (sample) — ammonium (indicator) in Table V. The graphs are of the type shown in Fig. 3. The straight-line portion of the titration curve (gas evolution due to reaction 5) is extended to intersect the abscissa. The intersection of the two lines marks the end-point of the reaction of arsenite with hypobromite.

TABLE V

TITRATION OF ARSENITE SOLUTION WITH CALCIUM HYPOCHLORITE SOLUTION

ml AsO_3^{-3} taken	*ml 0.1M $Ca(ClO)_2$ consumed*		
	Procedure 4	Indicator method[7]	Δ%
5.00	2.08		
5.00	2.14		
5.00	2.12		
	mean 2.11	mean 2.11	0.00

Reagents

Calcium hypochlorite, 0.1*M* solution.
Arsenite solution.
Ammonium sulfate 0.1*M* solution.
Sodium hydrogen phosphate, concentrated solution neutral to phenolphtalein.
Potassium bromide, solid.

Procedure 4

Transfer 5.00 to 10.00 ml of the neutral or alkaline arsenite solution to the titration flask, add about 5 ml of ammonium sulfate solution, 2 ml of phosphate buffer and some potassium bromide. Titrate with standard calcium hypochlorite solution, following the general instructions given in *Procedure* 1. The determination of three or four points during the gas evolution reaction is sufficient to locate the end-point.

DETERMINATION OF NITRITE AND NITRATE

In a previous paper[8] we described a method for the determination of nitrate, based on the titration of the excess sulfamic acid left over in the reaction:

$$HNO_3 + H_2N.SO_3H \rightarrow N_2O + H_2SO_4 + H_2O \quad . \; . \; . \quad (6)$$

with standard nitrite solution:

$$NaNO_2 + H_2N.SO_3H \rightarrow N_2 + NaHSO_4 + H_2O \quad . \; . \; . \quad (7)$$

Reaction (7) can be used also for the determination of nitrite ion by the gas pressure end-point technique[8] and is therefore of importance in the analysis of both nitrate and nitrite.

TABLE VI

TITRATION OF SULFAMIC ACID SOLUTION WITH SODIUM NITRITE SOLUTION

ml $0.1M$ $H_2N.SO_3H$ *taken*		*ml* $0.1M$ $NaNO_2$ *consumed*		
		Procedure 5	External indicator method[11]	Δ%
5.00		5.17		
5.00		5.19		
5.00		5.18		
	mean	5.18	5.20	−0.38

Table VI summarizes the results obtained with the graphical method of end-point detection in the gasometric titration of sulfamic acid with nitrite solution. The graphs are of the type shown in Fig. 2.

Reagents

Sodium nitrite, approx. 0.1M solution.
Sulfamic acid, approx. 0.1M solution.

Procedure 5

Transfer 5.00 to 10.00 ml of the sulfamic acid solution to the titration flask and titrate with sodium nitrite solution, following the general instructions outlined in *Procedure* 1

TITRATION OF HYDROXIDE WITH ACID

In a previous paper[9] the titration of an alkali hydroxide solution with acid to the gas pressure end-point was described. Table VII gives results obtained with the graphical method of end-point detection in this titration. The graphs are of the type shown in Fig 3. The intersection of the lines corresponding to the main reaction (no gas evolution) and the secondary reaction (carbon dioxide evolution) signals the end-point.

TABLE VII

TITRATION OF SODIUM HYDROXIDE SOLUTION WITH HYDROCHLORIC ACID SOLUTION

ml NaOH taken		*ml* $0.1N$ *HCl consumed*		
		Procedure 6	Indicator phenolpht.	Δ%
5.00		5.56		
5.00		5.58		
5.00		5.60		
5.00		5.58		
	mean	5.58	5.58	0.00

Reagents

Sodium hydroxide solution.
Hydrochloric acid, 0.1N solution.
Sodium bicarbonate, solid.

Procedure 6

Transfer 5.00 to 10.00 ml of the hydroxide solution to the titration flask, add a small quantity of sodium bicarbonate and titrate with the acid solution, following the general instructions given in *Procedure* 1. The determination of 3 or 4 points during the gas evolution reaction is sufficient to locate the end-point.

TITRATION OF CARBONATE WITH ACID

In a previous paper[9] the titration of an alkaline carbonate solution with acid to the gas pressure end-point was described. Tables VIII and IX give results obtained with the graphical method of end-point detection in this titration. The graphs are of the type shown in Fig. 4. The intersection of the lines corresponding to the first reaction (no gas evolution) and to the second reaction (carbon dioxide evolution) gives the volume of acid required to transform all the carbonate present in bicarbonate. The intersection of the lines corresponding to the second reaction (carbon dioxide evolution) and to the excess titrant gives the volume of acid required to destroy all of the bicarbonate.

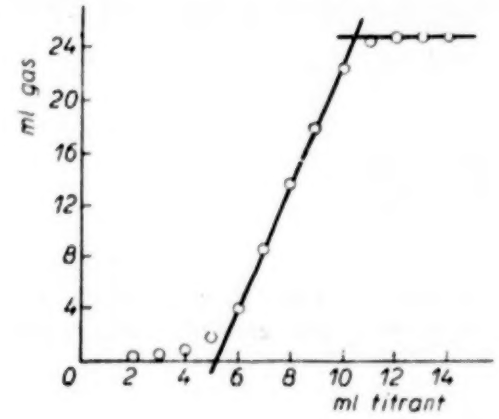

Fig. 4. Gasometric titration of 5.00 ml 0.5000N Na_2CO_3 solution with 0.25N HCl solution. First end-point 5.20 ml (calculated 10.42:2 = 5.21 ml). Second end-point 10.42 ml (indicator methyl orange 10.42 ml).

TABLE VIII

TITRATION OF SODIUM CARBONATE SOLUTION WITH HYDROCHLORIC ACID SOLUTION

ml 0.1N technical Na_2CO_3 taken	*ml 0.1000N HCl consumed*					
	First end-point			*Second end-point*		
	Procedure 7	Indicator phenolpht. with reference solution[12]	Δ %	Procedure 7	Indic. methyl orange	Δ %
5.00	2.02			4.88		
5.00	2.02			4.85		
5.00	2.09			4.89		
	mean 2.04	mean 2.06	−0.97	mean 4.87	mean 4.88	−0.20

TABLE IX

TITRATION OF SODIUM CARBONATE SOLUTION WITH HYDROCHLORIC ACID SOLUTION

ml 0.5000N pure Na_2CO_3 taken	*ml 0.25N HCl consumed*					
	First end-point			*Second end-point*		
	Procedure 7	Calculated	Δ %	Procedure 7	Indic. methyl orange	Δ %
5.00	5.21			10.42		
5.00	5.20					
5.00	5.17			10.46		
5.00	5.22					
	mean 5.20	10.42:2=5.21	−0.19	mean 10.44	mean 10.42	+0.19

Reagents

Sodium carbonate, technical, approx. 0.1*N* solution.
Hydrochloric acid, 0.1000*N* solution.
Sodium carbonate, pure[10], 0.5000*N* solution.
Hydrochloric acid, approx. 0.25*N* solution.

Procedure 7

Transfer 5.00 to 10.00 ml of the carbonate solution to the titration flask and titrate with the acid solution, following the general instructions outlined in *Procedure* 1.

Precision and accuracy

The results reported in Tables I-IX show, that with regard to precision and accuracy the gasometric titrations are comparable to the conventional visual end-point titrations.

A factor which affects considerably the precision of the results is the scale of the graphs. In all experiments of the present study "millimeter paper" was used, 5 cm on the abscissa representing 1 ml of titrant and 1 cm on the ordinate representing 1 ml of gas. Another factor of importance to precision is the volume of the gas bubbles and hence the diameter of the capillary from which they emerge. For titrations involving 0.1*N* solutions the diameter should not be greater than 1 mm.

Speed of titration

For all reactions studied in this work 2 minutes efficient stirring is ample to expel the gas formed by 1 ml of 0.1*N* titrant (3 minutes per 1 ml of 0.25*N* acid). In rapid reactions (*e.g.* nitrite and sulfamic acid, azide and ceric ion) this figure can be reduced to 1 minute. Since half a dozen increments of titrant are sufficient to establish the end-point, the total duration of a titration is 6 to 12 minutes.

DISCUSSION

The gas pressure end-point technique was originally developed as a simple means of titrating solutions which for any reason cannot be titrated to a visual end-point. The present paper broadens the scope of the original work, contributing also to the domain of gasometric methods. In fact, it should be possible to perform many gasometric analyses by the graphical technique described in the present paper. One of the greatest advantages of those methods — the fact that the reagent need not be of exactly known concentration — would thus be lost but many of the hazards and drawbacks would be eliminated. Thus the proposed technique does not depend to a high degree on a perfectly leakless apparatus. Furthermore neither temperature nor pressure need to be taken into account in the computation of the results, no calculation being required. The solutions and the interior of the apparatus need not be air free. The gas or gases evolved need not be purified or separated.

Gasometric titration curves can furnish information about the composition or the purity of the sample which neither a conventional indicator titration nor a gasometric method can give. Generally speaking, any irregularity of the titration curve is caused by another substance or substances capable of reaction with the titrant. A few binary mixtures were examined. They can be divided in two categories:

1) Both substances produce gases with the titrant.

a) Equal quantities of titrant release the same quantity of gas from the two substances. Only the sum of the two substances can be determined, since only one straight line will be obtained. Should the rate of reaction of the two substances be very different, a break in the curve can be obtained after the first more rapid reaction, if the time interval between addition of the titrant and observation of the gas volume evolved, is not long enough to allow the collection of the whole quantity of gas due to the second slow reaction.

b) Equal quantities of titrant release different quantities of gas from the two substances. If the rate of reaction of the two substances with the titrant is different, a break in the titration curve will be obtained. The greater the difference in the velocities of the reactions, the better the accuracy of the first end-point. The greater the difference of gas volume released by the two substances (and hence the greater the difference in the slopes of the two straight-line portions of the curve), the better the precision of the first end-point. Representative titration curves of two systems studied are shown in Fig. 5 and 6. The difference in reaction velocities in neither case is sufficient to permit the detection of the first end-point with reasonable accuracy.

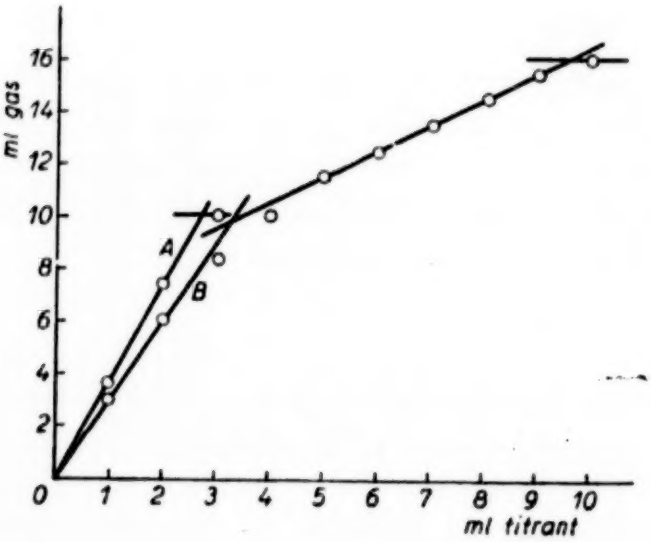

Fig. 5.

A. Gasometric titration of 2.50 ml NaN_3 solution with $0.1N$ $[Ce(NO_3)_6](NH_4)_2$ solution.
End-point 2.73ml (color end-point 2.74ml).

B. Gasometric titration of 2.50 ml of the same NaN_3 solution + 2.50 ml $N_2H_4 \cdot H_2SO_4$ solution with the same titrant.
First end-point (reaction 2) 3.18 ml (expected, see curve A, 2.73 ml).
Second end-point (reactions 1 and 2) 9.57 ml (color end-point 9.55 ml).

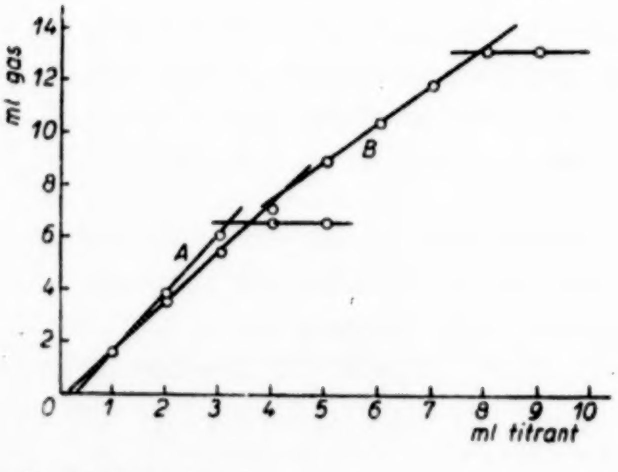

Fig. 6.

A. Gasometric titration of 2.00 ml $N_2H_4 \cdot H_2SO_4$ solution (+ 2 ml phosphate buffer + KBr) with $0.1304M$ $Ca(ClO)_2$ solution.
End-point 3.20 ml (color end-point 3.20 ml).

B. Gasometric titration of 2.00 ml of the same $N_2H_4 \cdot H_2SO_4$ solution + 2.00 ml $(NH_4)_2SO_4$ solution (+ 2 ml phosphate buffer + KBr) with the same titrant.
First end-point 4.10 ml (expected, see curve A, 3.20 ml).
Second end-point 7.92 ml (color end-point 7.94 ml).

2) Only one of the substances produces gases with the titrant.

a) The reaction of the substance which produces a gas with the titrant is slower than the other one as in the titrations of hydroxide — bicarbonate with acid (Table VII), arsenite — ammonium with hypochlorite (Table V) and ferrous — hydrazine with tetrapositive cerium (Table II).

b) The reaction rates are not sufficiently different. Such a case is exemplified by the titration of hydrogen peroxide — sulfamic acid with nitrite (Fig. 7).

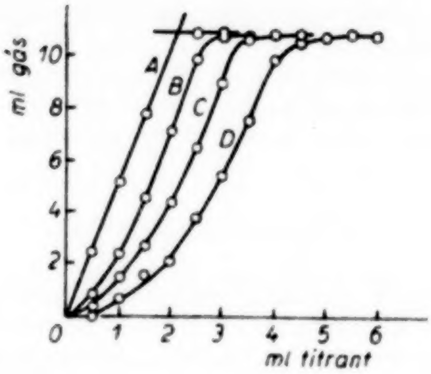

Fig. 7.

A. Gasometric titration of 2.50 ml $H_2N.SO_3H$ solution with 0.2*M* $NaNO_2$ solution. End-point 2.09 ml (color end-point[11] 2.10 ml).
B. Gasometric titration of 2.50 ml of the same $H_2N.SO_3H$ solution + 5.00 ml of H_2O_2 solution.
C. *Idem* + 10.00 ml of the same H_2O_2 solution.
D. *Idem* + 15.00 ml of the same H_2O_2 solution.

The proposed technique can be used in reactions which proceed sluggishly near the end-point. In such cases readings may be taken well before and well after the equivalence point, thus ensuring in both cases a reasonable excess of one of the reagents.

ACKNOWLEDGEMENT

The author is indebted to Dr. TAYGOARA FLEURY DE AMORIM, director of the Instituto de Química Agrícola, for the opportunity of carrying out this work at the Institution, and to the Conselho Nacional de Pesquisas for financial support.

SUMMARY

It was shown in previous papers, that many titrimetric problems can be solved by observing the pressure change of a closed system above the solution titrated at the equivalence point. This principle was made the basis of a gasometric titration method in which the end-point is found graphically. The titrant is added to the sample solution in measured increments at fixed intervals of time and the corresponding gas pressure or volume of the system is recorded and then plotted against the volume of added titrant. Half a dozen readings are sufficient to establish the end-point of a titration, which is found at the intersection of two straight lines. This graphical method was applied to cerimetry and chlorometry, as well as to some other analytical reactions (determination of nitrite, nitrate, hydroxide and carbonate) already described in previous papers on the gas pressure end-point technique. The results are comparable in precision and accuracy to the values obtained by the conventional visual end-point titrations. A gasometric titration takes about 10 minutes. The presence of other substances in the sample capable of reacting with the titrant does not necessarily cause interference.

RÉSUMÉ

Il a été démontré dans des articles précédents que beaucoup de problèmes titrimétriques peuvent être résolus en observant le changement de pression produit au point d'équivalence dans un système fermé au-dessus de la solution titrée. Ce principe est à la base d'une méthode de titration gazométrique dans laquelle le point final est déterminé graphiquement. Le réactif titrant est ajouté à la solution à analyser, par portions successives, à intervalles de temps fixes; la pression de gaz correspondante (ou volume du système) est enregistrée. Cette pression (ou volume) est ensuite rapportée au volume du réactif ajouté. Six lectures sont suffisantes pour déterminer le point final d'une titration, obtenu par l'intersection de deux droites. Cette méthode graphique a été appliquée à la cérimétrie et à la chlorométrie, de même qu'à quelques autres réactions analytiques (détermination des nitrites, nitrates, hydroxydes et carbonates) déjà décrites dans des articles précédents, sur la technique utilisant la pression gazeuse pour la détermination du point d'équivalence. Les résultats sont comparables, comme précision et exactitude, aux valeurs obtenues par les méthodes usuelles. Une titration gazométrique nécessite environ 10 minutes. La présence d'autres substances pouvant réagir avec le réactif ne gêne pas forcément.

ZUSAMMENFASSUNG

In vorhergehenden Artikeln wurde gezeigt, dass viele titrimetrische Probleme gelöst werden können, durch Beobachtung der Druckänderung am Umschlagspunkt in einem geschlossenen System über der titrierten Lösung. Dieses Prinzip bildet die Grundlage einer Methode der gasometrischen Titration, in welcher der Endpunkt graphisch bestimmt wird. Das zur Titration verwendete Reagenz wird zu der zu bestimmenden Lösung in hintereinanderfolgenden Zugaben in bestimmten Zeitabständen gegeben. Der entsprechende Gasdruck (oder das Volumen des Systems) wird registriert. Dieser Druck (oder Volumen) wird darauf auf das Volumen des dazugegebenen Reagenzes zurückgeführt. Sechs Ablesungen sind ausreichend, um den Endpunkt einer Titration zu bestimmen, welchen man durch den Schnitt zweier Geraden erhält. Diese graphische Methode wurde auf die Cerimetrie, auf die Chlorometrie sowie auch auf einige andere analytische Reaktionen (Bestimmung von Nitriten, Nitraten, Hydroxyden und Karbonaten) die schon in früheren Artikeln über die Technik durch Gasdruck den Gleichgewichtspunkt zu bestimmen beschrieben wurden, angewendet. Die Resultate sind in Bezug auf Präzision und Exaktheit mit den Werten der üblichen Methoden vergleichbar. Eine gasometrische Titration dauert ungefähr 10 Minuten. Die Gegenwart anderer Substanzen, welche mit dem Reagenz reagieren könnten, stört nicht unbedingt.

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A FERRICYANIDE-CERIOMETRIC DETERMINATION OF VANADIUM

by

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PALMER[1] first studied the oxidation of vanadyl ion by alkaline ferricyanide and adopted this redox reaction for the quantitative estimation of vanadium. An aqueous solution of ammonium vanadate was reduced by sulphur dioxide and the blue vanadyl compound was reoxidized by potassium ferricyanide in strongly alkaline medium. The resulting vanadic acid was removed by precipitating as barium vanadate and the ferrocyanide in the filtrate was titrated with a standard solution of permanganate in hydrochloric acid medium. This method, however, necessitated the addition of a minimum ten-fold excess of ferricyanide and was found to be impracticable for accurate routine work. Further, it was observed that in the titration of ferrocyanide against $KMnO_4$ the perception of the correct end-point was difficult, presumably owing to the formation of the sparingly soluble potassium manganous ferrocyanide[2,3]. It is well known that ceric sulphate is a powerful oxidizing agent and its solutions, as compared with permanganate and other familiar oxidants used in quantitative analysis, are remarkably stable on standing and even on boiling[4]. A reinvestigation of PALMER's method of estimating vanadium, using $Ce(SO_4)_2$ in place of $KMnO_4$ for the titration of ferrocyanide, was therefore thought desirable. This modified procedure is here reported in some detail.

EXPERIMENTAL

E. Merck's guaranteed sample of vanadyl sulphate was used to prepare a stock solution and its vanadium content was determined by the classical $KMnO_4$ method[5].

An approximately 0.1 N solution of $K_3[Fe(CN)_6]$ was obtained by dissolving a requisite quantity of the E. Merck's extra pure crystals in water. Ceric sulphate solution was prepared by digesting in concentrated sulphuric acid a 40% commercial sample of CeO_2, as recommended by WILLARD AND YOUNG[6]. Its strength was determined by titration with standard Mohr's salt solution using ferroin indicator[7].

To an aliquot volume of vanadyl sulphate solution taken in a 350 ml Erlenmeyer flask, a known excess of $K_3[Fe(CN)_6]$ solution and a requisite quantity of sodium hydroxide to maintain its overall normality in the system between 0.5-1 N were added. The contents of the flask were left to stand for about half an hour and then diluted to 250 ml in a standard flask. A measured volume of this solution was acidified gradually by adding dilute sulphuric acid (1:3) till a green precipitate appeared and the ferrocyanide was then titrated against standard ceric sulphate using ferroin or 1-2 drops of $FeCl_3$ (towards the end) as the indicator[8].

The amount of vanadium in a given solution was calculated in accordance with the following equations:

$$2K_3[Fe(CN)_6] + 2KOH \rightarrow 2K_4[Fe(CN)_6] + H_2O + [O] \quad \ldots\ldots \quad (1)$$

$$2VOSO_4 + 3H_2O + [O] \rightarrow 2HVO_3 + 2H_2SO_4 \quad \ldots\ldots \quad (2)$$

$$2Ce(SO_4)_2 + 2K_4[Fe(CN)_6] \rightarrow 2Ce_2(SO_4)_3 + 2K_3[Fe(CN)_6] + K_2SO_4 \quad \ldots \quad (3)$$

Thus 1 $VOSO_4 \equiv 1K_4[Fe(CN)_6] \equiv 1Ce(SO_4)_2$ or 1 ml of 1*N* $Ce(SO_4)_2$ corresponds to 0.05095 g of vanadium. A representative set of results is entered in Table I.

TABLE I

Expt. No.	*Vol. of $VOSO_4$ (ml)*	*Strength of $Ce(SO_4)_2$ (N)*	*Vol. of $Ce(SO_4)_2$ ≡ ferrocyanide formed (ml)*	*Vanadium (g)* By $KMnO_4$ a	*Vanadium (g)* By $Ce(SO_4)_2$ b	*Diff. a ~ b*
1	5	0.04281	10.45	0.02283	0.02279	0.00004
2	10	0.04281	21.00	0.04566	0.04566	0.00014
3	20	0.1061	16.90	0.09132	0.09135	0.00003
4	25	0.1061	21.10	0.11415	0.1140	0.00015
5	30	0.1061	25.40	0.1370	0.1373	0.00030
6	40	0.1061	34.00	0.18264	0.1838	0.00116
7	50	0.1061	42.25	0.2283	0.2283	nil
8	60	0.1061	50.50	0.27396	0.2730	0.00096

TABLE II

Expt. No.	*$K_3[Fe(CN)_6]$ added (g)*	*Overall alkalinity (N)*	*Vol. of 0.04281N $Ce(SO_4)_2$ ≡ ferrocyanide formed (ml)*	*Vanadium (g)* By $KMnO_4$ a	*Vanadium (g)* By $Ce(SO_4)_2$ b	*Diff. a ~ b*
1	0.5083	1.0	21.00	0.04566	0.04580	0.00013
2	1.0166	1.0	21.05	0.04566	0.04590	0.00024
3	1.5249	1.0	21.00	0.04566	0.04580	0.00013
4	3.0498	1.0	21.00	0.04566	0.04580	0.00013
5	0.5083	0.50	21.00	0.04566	0.04580	0.00013
6	0.5083	0.83	20.95	0.04566	0.04568	0.0002
7	0.5083	1.25	21.00	0.04566	0.04580	0.00013
8	0.5083	1.50	20.80	0.04566	0.04536	0.00030
9	0.5083	2.0	20.85	0.04566	0.04547	0.00019

Experiments performed with varying quantities of potassium ferricyanide revealed that the oxidation of vanadyl ion is complete even with 1½-2 fold excess of the oxidant, and the addition of a large excess of ferricyanide as reported by PALMER (*loc. cit.*), although without any adverse effect, is not essential (*cf.* Table II). Furthermore, the amount of sodium hydroxide added is not critical and the reaction proceeds quantitatively over a fairly wide range of alkali concentration. The present method of estimating vanadium is therefore more simple, accurate and broad-based than the one adopted by PALMER.

ACKNOWLEDGEMENTS

Sincere thanks of the author are due to Professor S. S. JOSHI for facilities and kind interest in the work. The award of a Scientific Man Power Committee Research Fellowship is also gratefully acknowledged.

SUMMARY

Oxidation of vanadyl ion by alkaline ferricyanide has been reinvestigated and a modified procedure for the volumetric estimation of vanadium, based on the titration of the resulting ferrocyanide against standard ceric sulphate, is described.

RÉSUMÉ

L'oxydation de l'ion vanadyle par une solution alcaline de ferricyanure a été étudiée. Une méthode est décrite pour le dosage volumétrique du vanadium; elle est basée sur la titration du ferrocyanure formé au moyen d'une solution étalon de sulfate de cérium(IV).

ZUSAMMENFASSUNG

Die Oxydation des Vanadylions mit einer alkalischen Ferricyanid-Lösung wurde studiert. Es wird eine Methode beschrieben, um Vanadin volumetrisch zu bestimmen. Sie basiert auf der Titration des Ferrocyanids, welches mit Hilfe einer Vergleichslösung von Cer(IV)-sulfat gebildet wird.

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TITRATIONS WITH EXTRACTIVE END-POINTS
III. THE IODINE TITRATION

by

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INTRODUCTION

The triphenylmethylarsonium cation has been applied to permanganate[1], and dichromate[2] titrations, using extractive end-points. This paper deals with its application (as triphenylmethylarsonium iodide) to the titration of arsenite and thiosulphate with iodine, and the reverse.

A convenient method of estimating iodine is by titration with standard thiosulphate or arsenite, using starch as indicator. Though the blanks for $N/10$ iodine are negligible[3] the use of starch as indicator suffers from a number of disadvantages, the chief being: (I) It gives a water-insoluble complex with iodine. (II) There is a drift end-point, which is marked when the solutions are dilute. (III) The end-point is not visible in the presence of large quantities of coloured ions. (IV) Starch cannot be employed in alcoholic solutions nor strongly acid solutions due to hydrolysis.

Extraction of iodine into carbon tetrachloride or chloroform at the end-point is an alternative method of titration[4]. Potentiometric determination of the end-point is successful in the thiosulphate/iodine titration[4,5], but not in the arsenite/iodine titration, as the redox potentials of oxidant and reductant are too close.

Coloured solutions may be titrated with iodine using the potentiometric method, or visually, using trypflavin as indicator[7] or extracting the iodine with carbon tetrachloride. In this paper, a new method is suggested for the titration of coloured solutions with iodine, in which the end-point is indicated by the extraction of yellow-brown Ph_3MeAsI_3 into an organic solvent layer. This method is applicable to the arsenite titration, there is no limit to the depth of colour of the aqueous layer, and the Ph_3MeAsI_3 is non-volatile.

DISCUSSION

Triphenylmethylarsonium tri-iodide, Ph_3MeAsI_3(I) has been prepared according to STEINKOPF AND SCHWEN[8] and also by the addition of iodine to triphenylmethylarsonium iodide. (I) is insoluble in ether and water but readily soluble in chloroform, ethylene dichloride, tetrachloroethane, carbon tetrachloride, chlorbenzene and boiling alcohol.

Iodine titrations with (I) as indicator are similar to the permanganate[1] and dichromate[2] titrations, except that the $Ph_3MeAs_3^+$ ion is added as a 1% aqueous solution of Ph_3MeAs I. The yellow-brown colour of (I) in the organic layer is readily seen against a white background and is not affected by coloured ions in the aqueous layer.

The method was applied to the titration of arsenite (Table I) and thiosulphate (Table II) with iodine solutions (*N*/10, *N*/50 and *N*/100). Blanks were negligible for *N*/10, 0.02 ml for *N*/50 and 0.04 ml for *N*/100 iodine. The reverse titrations were also successful, the end-point being indicated by the disappearance of colour in the organic layer. The blanks were similar (*N*/10 iodine: 0.01 ml; *N*/50 iodine: 0.04 ml; *N*/100 iodine: 0.06 ml). Large concentrations (up to 200:1) of chromium (III), nickel (II), cobalt(II) and manganese(II) were without effect in titrations of thiosulphate with iodine (Table I). In the case of titrations of arsenite with iodine, nickel (II), manganese(II) and cobalt(II) were precipitated, probably as basic carbonates. These precipitates fell into the organic layer, making it impossible for the end-point to be observed; chromium(III) did not precipitate and did not interfere (Table II). Copper(II) ions liberate iodine from the iodide ions present[9] and so were not tested for interference.

Chloroform, carbon tetrachloride and chlorbenzene were satisfactory extractants for (I), but the partition coefficient of ethylene dichloride was too high, giving a titration error of -0.1 ml for *N*/10 solutions.

The method could not be applied to the determination of copper by the liberation of iodine from iodide ions[10], as the precipitated cuprous iodide fell into the organic layer. Attempts to filter off the cuprous iodide before titration were not successful.

Procedure

The titrations were carried out in a special stoppered flask (500 ml); as previously described in Part I.

In all cases 25 ml aliquots of solution were pipetted into the flask and then the 1% aqueous Ph_3MeAsI (0.5 ml) added, together with 5 ml of chloroform or carbon tetrachloride. The conditions of pH and volume were identical with those described for the standard arsenite[11] and thiosulphate[12] titrations. The interfering cations were added as their sulphates dissolved in water (*ca.* 100 ml). The iodine solution was added dropwise with shaking near the end-point, which was indicated by the colourless organic layer turning yellow-brown.

EXPERIMENTAL

Triphenylmethylarsonium tri-iodide (I), Ph_3MeAsI_3. This was made by two methods.

(i) Prepared according to STEINKOPF AND SCHWEN[8] by the dropwise addition of iodine in dry light petroleum to triphenylarsine in dry light petroleum. The resulting unstable di-iodo triphenylarsine was then refluxed with methyl iodide for 3 hours. On cooling the tri-iodide separated as a brown oil which soon crystallized.

$$Ph_3As + I_2 \longrightarrow Ph_3AsI_2$$
$$Ph_3AsI_2 + MeI \longrightarrow Ph_3MeAsI_3$$

Overall yield = 54%.

(I) was recrystallized from aqueous alcohol, as lustrous brown leaflets, m.p. 107-8° (d); literature[6] reports m.p. 107° (d).

(ii) Triphenylmethylarsonium iodide (9.0 g) was dissolved in alcohol (100 ml) and iodine (5.1 g) in alcohol (100 ml) added dropwise to the boiling solution, and then the solution refluxed for 30 minutes. Water was added to the boiling solution and let cool. Brown leaflets of (I) separated.

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(I) was collected, washed with aqueous alcohol and recrystallized from aqueous alcohol, m.p. 106-9° (d). The melting point was not depressed with a sample of (I) made by method (i).

$$\mathrm{Ph_3MeAsI} + \mathrm{I_2} \rightarrow \mathrm{Ph_2MeAsI_3}$$
$$\text{yield} = 96\%.$$

The iodine was determined by the method of DWYER AND NYHOLM[13].

Found: I = 54.21%, 54.15%
$\mathrm{Ph_3MeAsI_3}$ requires: I = 54.25%.

RESULTS

N/10, *N*/50 and *N*/100 solutions of iodine[14], arsenite[11] and thiosulphate[15] were prepared.

Solvent: Carbon tetrachloride (5 ml)
Volume of 1% $\mathrm{Ph_3MeAsI}$ solution = 0.5 ml

TABLE I

N/10, *N*/50 and *N*/100 sodium thiosulphate (25 ml) with iodine. Results by extractive method compared with those by potentiometric[4,5] and starch indicator methods.

Interfering ion	*Molar ratio ion: iodine*	*Concentration of iodine*	*Mean titration (ml)*		*Starch*
			Potentiometric	*Extractive*	
Cr^{+3}	100:1	*N*/10	24.47	24.48	•
Cr^{+3}	200:1	*N*/50	24.91	24.92	•
Cr^{+3}	200:1	*N*/100	25.20	25.19	•
Ni^{+2}	100:1	*N*/10	24.50	24.50	•
Ni^{+2}	200:1	*N*/50	24.91	24.91	•
Ni^{+2}	200:1	*N*/100	25.20	25.21	•
Co^{+2}	100:1	*N*/10	24.49	24.49	•
Co^{+2}	200:1	*N*/50	24.89	24.91	•
Co^{+2}	200:1	*N*/100	25.21	25.20	•
Mn^{+2}	100:1	*N*/10	24.50	24.49	24.48
Mn^{+2}	200:1	*N*/50	24.90	24.89	24.91
Mn^{+2}	200:1	*N*/100	25.21	25.21	25.23

• End-point not visible, due to coloured ions present.

TABLE II

N/10, *N*/50 and *N*/100 arsenite solutions (25 ml) with iodine.

Interfering ion	*Molar ratio ion: iodine*	*Concentration of iodine*	*Mean titration (ml)*	
			Extractive	*Starch*
Cr^{+3}	100:1	*N*/10	25.12	25.12••
Cr^{+3}	200:1	*N*/50	25.24	25.23••
Cr^{+3}	200:1	*N*/100	25.17	25.18••

•• Titration results in absence of chromium(III) ions; as in Table I the end-point could not be seen when chromium(III) was present.

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SUMMARY

A method for the titration of arsenite and thiosulphate with iodine is recommended in which the iodine is extracted as Ph_3MeAsI_3 at the end-point. The method is satisfactory for titration with *N*/10, *N*/50 and *N*/100 iodine solutions, in the presence of coloured ions of molar concentrations up to 200 times that of the iodine solution. Copper(II) ions interfere. A stable tri-iodide Ph_3MeAsI_3 has been prepared by two different methods.

RÉSUMÉ

Une méthode de dosage titrimétrique de l'arsénite et du thiosulfate par l'iode est recommandée; au point d'équivalence, l'iode est extrait comme Ph_3MeAsI_3. Ce dosage peut être effectué avec des solutions d'iode *N*/10, *N*/50 et *N*/100, en présence d'ions colorés, en concentrations molaires allant jusqu'à 200 fois celle de la solution d'iode. Les ions cuivre(II) gênent. Un tri-iodure stable Ph_3MeAsI_3 a été préparé par deux méthodes différentes.

ZUSAMMENFASSUNG

Es wird eine Methode zur titrimetrischen Bestimmung von Arsenit und Thiosulfat mit Jod empfohlen. Am Gleichgewichtspunkt wird das Jod als Ph_3MeAsJ_3 ausgezogen. Diese Bestimmung kann mit *N*/10, *N*/50 und *N*/100 Jodlösungen in Gegenwart von gefärbten Ionen von molaren Konzentrationen, die bis zu 200 Mal grösser sind, als die der Jodlösung, ausgeführt werden. Die Kupfer(II)-Ionen stören. Es wurde ein stabiles Trijodid Ph_3MeAsJ_3 nach zwei verschiedenen Methoden hergestellt.

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THE THERMOLYSIS OF THE NEOCUPFERRON CHELATES OF YTTRIUM AND THE RARE EARTH ELEMENTS

by

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Neocupferron (ammonium salt of α-naphthyl-N-nitrosohydroxylamine) was proposed by BAMBERGER AND BAUDISCH[1] as a precipitant for iron(III). DUVAL[2] studied the thermolysis curve for this chelate and found it was stable up to 101°. Beyond this temperature the organic material was destroyed with the oxide level appearing above 754°. Similar results were obtained with the neocupferron chelate of copper(II), the chelate being less stable than iron(III)[3].

The use of neocupferron as a precipitant for the rare earth elements has recently been proposed by POPOV AND WENDLANDT[4]. It was found that this reagent precipitated the rare earth ions quantitatively from a neutral or slightly acid solution. The resulting chelates were ignited at 900° to the corresponding rare earth oxides.

This study was undertaken to determine the exact temperature limits of the thermolysis curves and also to examine any intermediate compounds that may be formed during the decomposition.

EXPERIMENTAL

Chemicals

Neocupferron was obtained from the Matheson, Coleman and Bell Co., East Rutherford, N. J. It was used without further purification.

The rare earths were obtained as the oxides of greater than 99% purity from the Lindsay Chemical Co., West Chicago, Ill., and Research Chemicals, Inc., Burbank, Calif. Since the contaminants were other rare earth elements, no further purification was necessary.

Yttrium chloride of 99% purity was obtained from Research Chemicals, Inc., Burbank, Calif. All other reagents were of analytical grade.

Thermobalance

The construction and operation of the thermobalance has been described elsewhere[5]. Due to vibration effects and air currents, DUVAL found that the conversion of an analytical beam balance into a thermobalance made an unreliable instrument[6]. However, a thermobalance constructed from a torsion balance did not suffer from these disadvantages. The sample weight varied from 100-200 mg with an accuracy in weighing of ± 0.1 mg. The temperatures were recorded to ± 1°. The accuracy and reproducibility of the thermobalance agreed to within 1% of the Chevenard recording thermobalance as checked against the thermolysis of $Na_2HPO_4 . 12H_2O$. The heating rate on all samples was about 4.5°/min with a maximum temperature limit of 950°.

Preparation and thermolysis of the chelates

The neocupferron chelates were prepared as previously described[4]. The chelates were dried at room temperature (*ca.* 25°) for 24 h before pyrolysis on the thermobalance. Temperature-composition readings were taken on the thermobalance at 5-10° intervals, during periods of rapid weight loss, readings were taken at 2-4° intervals. The thermolysis curves are shown in Figs. 1 and 2. Each curve was repeated at least twice.

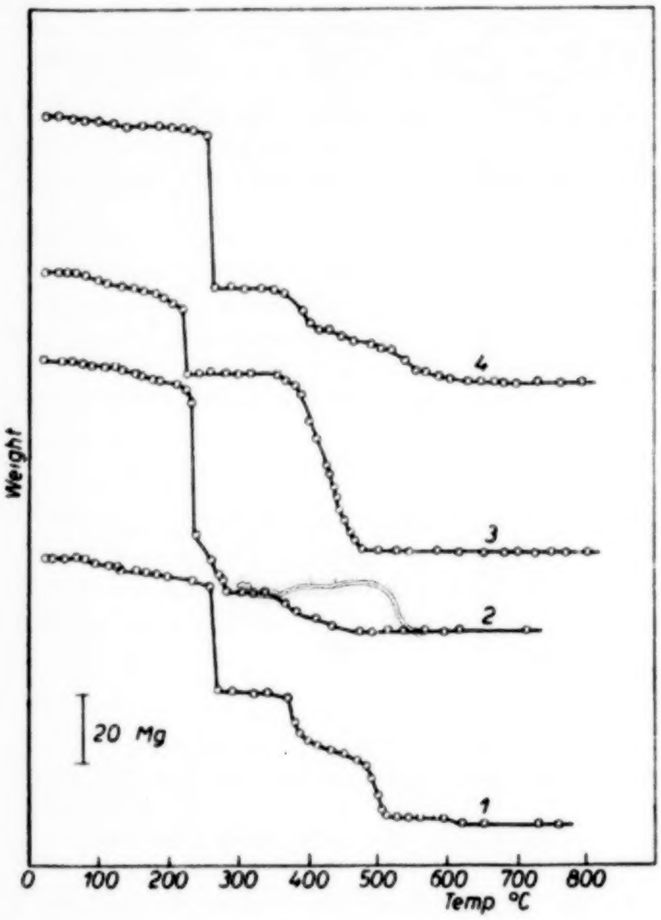

Fig. 1.

Thermolysis curves of the neocupferron chelates.
Curve 1. Lanthanum neocupferrate
2. Cerium(III) neocupferrate
3. Cerium(IV) neocupferrate
4. Praseodymium neocupferrate

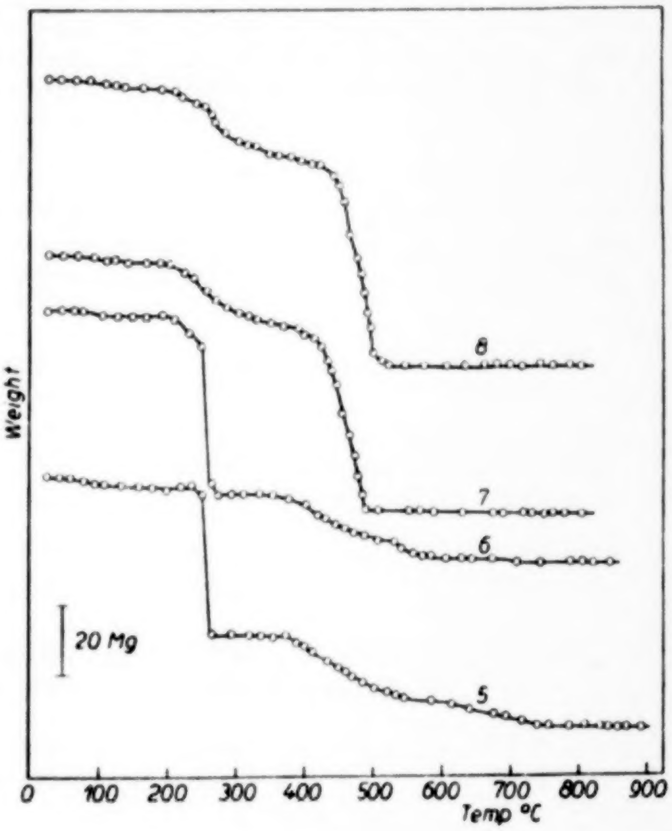

Fig. 2.

Thermolysis curves of the neocupferron chelates.
Curve 5. Neodymium neocupferrate
6. Samarium neocupferrate
7. Gadolinium neocupferrate
8. Yttrium neocupferrate

DISCUSSION

The neocupferron chelates of the rare earths are less stable than the corresponding iron(III) and copper(II) chelates. The thermolysis curves of lanthanum, praseodymium, neodymium and samarium chelates (group I) are similar while yttrium is identical with the gadolinium chelate (group II) curve. Cerium(III) and cerium(IV) are again different from the other two groups (group III).

In all three of the groups, the first decomposition occurred at about 80°. This decomposition resulted in the loss of a compound of molecular weight of about 18. Table I gives the data that compares the original molecular weight of the chelate with the molecular weight of the new compound formed at 80°. An average value, excluding the cerium(III) value, was about 18 ± 2. This would strongly suggest the loss of one molecule of water from the chelate. Yet, the molecular weight of the chelate indicates no water of hydration as did the original analysis made in the previous work[4]. The origin of this molecule of water, if it is water, must come from an intramolecular rearrangement in the chelate molecule.

TABLE I

COMPOSITION AND MOLECULAR WEIGHTS OF THE INTERMEDIATE NEOCUPFERRON CHELATES

A *Neocupferron chelate*	*B* *Percent oxide in chelate (found)*	*C* *Molecular weight of chelate (found)*	*D* *Percent oxide in chelate in second plateau (found)*	*E* *Molecular weight (found)*	*F* *Difference in molecular weight (C-E)*
Lanthanum	22.80%	714	23.30%	699	15
(calc.)	23.26	700.4			
Cerium (III)	22.21	775	23.86	721	(54)
(calc.)	24.53	701.6			
Cerium (IV)	16.43	853	—	—	—
(calc.)	19.37	888.8			
Praseodymium	24.08	707	24.91	683	24
(calc.)	24.24	702.4			
Neodymium	23.94	703	24.65	683	20
(calc.)	23.83	705.8			
Samarium	24.23	720	24.71	706	14
(calc.)	24.50	711.9			
Gadolinium	25.10	718	25.67	702	16
(calc.)	25.18	718.4			
Yttrium	17.84	632	—	—	—
(calc.)	17.36	650.4			
Average					18 ± 2

The compound formed at 80° is stable up to about 260° in group I where it proceeds to decompose into the corresponding rare earth oxides. In groups II and III, this intermediate compound was less stable, decomposing at about 210-220°.

The other intermediate compounds formed do not correspond to stoichiometric compositions and are probably mixtures of decomposition products.

The temperatures at which the oxide levels were reached are recorded in Table II.

TABLE II

OXIDE LEVEL TEMPERATURES

Neocupferron chelate	*Oxide*	*Temperature °C*
Lanthanum	La_2O_3	> 605
Cerium(III)	CeO_2	> 460
Cerium(IV)	CeO_2	> 488
Praseodymium	Pr_6O_{11}	> 648
Neodymium	Nd_2O_3	> 750
Samarium	Sm_2O_3	> 660
Gadolinium	Gd_2O_3	> 490
Yttrium	Y_2O_3	> 523

References p. 553.

The values ranged from a minimum of 460° in the case of cerium(III) to a maximum of 750° for neodymium. From this information, it hardly seems necessary to ignite the neocupferron chelates to 900° as previously described.

SUMMARY

The thermolysis curves of the neocupferron chelates of yttrium, lanthanum, cerium(III), cerium(IV), praseodymium, neodymium, samarium and gadolinium were determined. It was found that the chelates were stable up to 80°, with the oxide levels being reached at 460-750°.

RÉSUMÉ

Les courbes de thermolyse des chélates obtenus entre le néocupferron et les éléments suivants: yttrium, lanthane, cérium(III) et (IV), praséodyme, néodyme, samarium et gadolinium, ont été determinées. On a pu ainsi démontrer que ces chélates étaient stables jusqu'à 80°, le palier des oxydes étant atteint à 460-750°.

ZUSAMMENFASSUNG

Die thermolytischen Kurven der Neokupferron-Chelate folgender Metalle: Yttrium, Lanthan, Cer(III) und (IV), Praseodym, Neodym, Samarium und Gadolinium wurden bestimmt. Auf diese Weise konnte gezeigt werden, dass die Chelate bis zu 80° stabil waren. Die Stufe der Oxyde wurde bei 460-750° erreicht.

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KONZENTRIEREN ANORGANISCHER IONEN AUF PAPIER MITTELS ELEKTROPHORESE

von

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ZWECK DER UNTERSUCHUNG

Bei der Durchführung qualitativer Reaktionen auf Papier wird die Empfindlichkeit in erheblichem Masse beeinflusst durch die Oberfläche, die von der zur Verfügung stehenden Menge des nachzuweisenden Stoffes eingenommen wird. Die ,,Oberflächenkonzentration" lässt sich bei Tüpfelreaktionen öfters durch Aufbringen der zu prüfenden Lösung mittels einer Kapillare verbessern, bisweilen wird dadurch sogar die Grössenordnung der Empfindlichkeit einen Schritt weiter geführt. In der Papierchromatographie ist die Schwierigkeit, kleine Flecken herzustellen, eine sehr bekannte; schon beim Aufbringen erhält der Tüpfel eine ziemliche Grösse, und die Flecken der einzelnen Ionen werden bei der Herstellung des Chromatogrammes um so grösser je weiter sie gewandert sind; auch werden die Grenzen oft unscharf. Die Empfindlichkeit des Nachweises in Papierchromatogrammen ist dann auch im allgemeinen nicht sehr befriedigend. Weil überdies, wegen der Gefahr von Streifenbildung und von Verzerrung der Flecken, die totale Konzentration im ursprünglichen Tropfen nicht allzu gross sein darf, ist das Leistungsvermögen dieser Arbeitsweise zumal in dem Sinne gering, dass ,,Mikro"-Bestandteile nicht ohne weiteres gefunden werden können, wenn die Makro-Komponenten z.B. in hundert- oder mehrfacher Menge anwesend sind. Das Grenzverhältnis wird von Fall zu Fall verschieden sein, es liegt im allgemeinen aber nicht günstig.

Einige Autoren[1-3] haben die ,,Oberflächenkonzentration" im ursprünglichen Tüpfel vergrössert indem sie die Flüssigkeit im Papier während des langsamen Einfliessens verdampfen lassen. In dieser Weise bekommt der Flecken vor dem Chromatographieren immerhin noch einen Durchmesser von etwa 1 cm.

Es wäre zu erwarten, dass eine bedeutende Verschiebung der Nachweisbarkeitsgrenzen zu erreichen wäre, wenn es gelingen würde, die gesuchten Stoffe auf einer viel kleineren Oberfläche zu konzentrieren und damit die Intensität der Reaktion stark zu vergrössern.

GEWÄHLTE ARBEITSWEISE

In der anorganischen Analyse haben wir für viele Ionen eine merkliche Verbesserung erhalten können mittels Konzentrieren der Ionen um eine spitze Elektrode

Literatur S. 561.

herum. Zur Prüfung der erreichbaren Empfindlichkeit wurden mit einer Reihe von Ionen nachstehende Versuche vorgenommen.

25 μl der Versuchslösung wird auf das Papier gebracht und der Tüpfel in einem Luftstrome getrocknet. Dann wird das Papier leicht mit 2*N* Essigsäure besprüht, im Falle von Anionen wird meistens 2*N* Ammoniak verwendet. Das feuchte Papier wird auf eine Platte aus Perspex gelegt. Mittels einer Klemme wird ein kurzes Platindrähtchen von 0.3 mm Dicke aufrecht in den Flecken gestellt; die andere Elektrode ist ein Platindraht von 0.1 mm Dicke, der in einer Entfernung von 2 bis 3 cm auf das Papier gelegt, mit einem Streifen aus Perspex bedeckt und mit zwei Federn angedrückt wird. Je nach Bedarf wird die spitze Elektrode als Kathode oder als Anode gebraucht. Während 15 Minuten wird eine Spannung von 100 Volt angelegt, dann wird das Papier an der Luft getrocknet und der Nachweis durchgeführt.

Bei dieser Arbeitsweise werden die Ionen gewöhnlich nicht als Element an der Elektrode abgeschieden, weil sie nahe an der Elektrode auf die alkalische bezw. saure Zone stossen, die sich um die Kathode bezw. Anode herum ausbildet. Dadurch werden die meisten Ionen als Hydroxyd gefällt und werden sie bei der Nachweisreaktion gewöhnlich als ringförmiger Hof sichtbar.

In dieser Weise werden die Nachweisbarkeitsgrenzen für viele Ionen bis auf einige Tausendstel oder Hundertstel μg heruntergebracht. Öfters gelangt man so bis zu Konzentrationen von z.B. $1 : 10^6$ bis $1 : 10^7$ herab, in denen derartig kleine Mengen mittels anderer Techniken (Tüpfelplatte, Mikroskop) nicht mehr nachgewiesen werden können. Was die Anwendung auf Papierchromatogramme betrifft, möge bemerkt werden, dass bei den gebräuchlichen Arbeitsweisen in dieser Methodik weit grössere Konzentrationen notwendig sind.

EMPFINDLICHKEITEN

Zunächst seien für eine Reihe von Ionen kurz die verwendeten Reaktionen und die gefundenen Nachweisbarkeitsgrenzen angegeben. Immer wurde eine Menge von 25 μl Lösung auf das Papier gebracht und damit wie oben beschrieben vorgegangen. Fallweise notwendige Abweichungen von diesen Versuchsbedingungen sind bei den einzelnen Reaktionen angegeben. Das Papier war gewöhnlich Whatman Nr 1, bisweilen Schleicher und Schüll Nr 589[3]. Die Reagenzien wurden, wenn nicht anders erwähnt, mit einem dünnen Glasstäbchen in sehr kleinen Tropfen auf das Papier gebracht.

Kathodisch konzentriert wurden die Ionen:

Cd^{+2} *Reagens*[4]: Cadion 2 β, $1^0/_{00}$ in Alkohol mit 1 Tropfen NaOH 2*N* je 2 ml.
Reaktion: rosa Kreischen auf blauem Hintergrund.
Empfindlichkeit: 3 ng ($1 : 8 \cdot 10^6$).
Blindversuch: 1 ng (10^{-9}g).

Co^{+2} Störung durch Fe im Papier aufheben mit einem Tropfen Na_3PO_4 2%; trocknen lassen.
Reagens[5]: α-Nitroso-β-naphtol 1% in Alkohol, nachher NaOH 2*N*.
Reaktion: rotbrauner Flecken auf gelbem Hintergrund.
Empfindlichkeit: 1 ng ($1 : 2.5 \cdot 10^7$).

Cr^{+3} Überführung in CrO_4^{-2}: Na_3PO_4 2%; trocknen; 1 Minute mit Br_2 bedampfen, 1 Minute an der Luft belassen; alkoholische Phenollösung 5%.
Reagens[6]: Diphenylcarbazid $1^0/_{00}$ in Alkohol mit 2% H_2SO_4.
Reaktion: violettes Kreischen.

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Empfindlichkeit: auf S und S Nr 589^3: 2 ng (1 : $1.2\cdot10^7$); auf Wh Nr 1 ein Blindwert von ungefähr 10 ng.
Bemerkung: vom Rande her verfärbt sich der Reagensflecken nachher nach violett, auch in Abwesenheit von Cr.

Mn^{+2} NaOH 2*N*, Luftoxydation.
Reagens[7]: Tolidin 1% in Essigsäure 50%.
Reaktion: blaues Kreischen, das bald verschwindet.

Empfindlichkeit: 1 ng (1 : $2.5\cdot10^7$).

Ni^{+2} *Reagens*[8]: Dimethylglyoxim 1% in Alkohol; danach einige Minuten in NH_3-Dampf.
Reaktion: rosa Kreischen, deutlicher nach Spülen mit Wasser aus einer Kapillare.
Empfindlichkeit: 1 ng (1 : $2.5\cdot10^7$).

Pb^{+2} Als Nitrat verwendet.
Reagens[9]: Na-rhodizonat 1%.
Reaktion: rotes Kreischen.
Empfindlichkeit: 10 ng (1 : $2.5\cdot10^6$).
Blindversuch: 5 bis 10 ng.

Tl^{+} Sulfat.
Reagens[10]: Phosphomolybdänsäure in Wasser, gesättigt; danach 2 Tropfen HBr 48%.
Reaktion: Blaufärbung.
Empfindlichkeit: 30 ng (1 : $8\cdot10^5$).
Blindversuch: ungefähr 10 ng.

UO_2 $^{+2}$ *Reagens*[11]: Fluorescein 1‰ in Alkohol; danach bis zur völligen Entfärbung des Eisenfluoresceinates (das Papier enthält Spuren Fe) antüpfeln mit $Na_2S_2O_3$ 20%, das eine Spur Cu^{+2} enthält.
Reaktion: ziemlich grosser roter Kreis.
Empfindlichkeit: 20 ng (1 : $1.2\cdot10^6$).
Blindversuch: ungefähr 10 ng.

Fe^{+3} Die Essigsäure und das Wasser in dem sie gelöst war, waren zweimal in Quarzglas destilliert.
Papier: S und S Nr 589^3.
Reagens[12]: Phenanthrolin 1% mit Hydroxylammoniumchlorid 5% zusammen in Alkohol.
Reaktion: rosa Flecken.
Empfindlichkeit: 2 ng (1 : $1.2\cdot10^7$).
Blindversuch: 0.5 bis 1 ng.

Ag^{+} Das Papier wird mit 0.2*N* HNO_3 besprüht, weil das Ag^+ in 2*N* Essigsäure nicht wandert. Der Strom wird nur während 10 Minuten durchgeführt, weil das Papier mit dem starken Elektrolyt leicht verkohlt.
Reagens[13]: Dimethylaminobenzylidenrhodanin, gesättigt in Aceton; nachher bedampfen mit NH_3.
Reaktion: violetter Flecken.
Empfindlichkeit: 3 ng (1 : $8\cdot10^6$).

Anodisch konzentriert wurden die Ionen:

Au^{+3} *Spannung:* 200 V. Sprühen mit 2*N* Essigsäure anstatt 2*N* NH_3.
Reagens[14]: $TiCl_3$ 15%.
Reaktion: blauer Flecken.
Empfindlichkeit: 100 ng (1 : $2.5\cdot10^5$).

BO_3 $^{-3}$ *Spannung:* 200 V; es scheint dass das Anion nur langsam wandert.
Reagens[15]: Kurkumatinktur mit gleichem Volum 2*N* Salzsäure vermischt; dabei wird eine Fällung durch Zugeben von Alkohol wieder gelöst. Nach dem Aufbringen des Reagenzes, das Papier im Luftstrom von 100° C erhitzen bis die braune Farbe gerade in braungrau umgeschlagen ist; schliesslich spülen mit NaOH 1% aus einer Kapillare, bis ein Kreis von ungefähr 2 cm Durchmesser befeuchtet ist.
Reaktion: blaues Kreischen.
Empfindlichkeit: 3 ng (1 : $8\cdot10^6$).

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Br^- *Spannung:* 200 V. Sprühen mit 2*N* Essigsäure.
Reagens[16]*:* Fluorescein, gesättigt, in Aceton.
Arbeitsweise: ein Streifchen Papier S und S Nr 589[3], mit der Reagenslösung getränkt, wird auf den Flecken gelegt und die Anode durch dieses Papier in den Flecken gestochen. Nach dem Konzentrieren bedampfen mit NH_3.
Reaktion: roter Flecken im oberen Papier.
Empfindlichkeit: 10 ng ($1 : 2.5 \cdot 10^6$).
Blindversuch: bis 10 ng.

J^- *Reagens:* Stärke 5% mit KCNS 0.03%, letzteres zur Reduktion von an der Anode gebildetem JO_3^-; das Reagens ist vor dem Stromdurchgang aufzubringen wegen der Flüchtigkeit des Jods.
Reaktion: Blaufärbung, meistens schon nach einer Minute.
Empfindlichkeit: 100 ng ($1 : 2.5 \cdot 10^5$).

MoO_4^{-2} *Reagens*[17]*:* $SnCl_2$ 10% in 2*N* Salzsäure, 2 Minuten mit ein wenig Sn gekocht, dann wird in der abgekühlten Flüssigkeit 5% KCNS gelöst.
Reaktion: roter Flecken.
Empfindlichkeit: 10 ng ($1 : 2.5 \cdot 10^6$).

VO_3^- *Reagens*[18]*:* Tannin 5% in Wasser oder Alkohol. Kleiner Tropfen notwendig, weil das Vanadat leicht weggespült wird.
Reaktion: blauer Flecken.
Empfindlichkeit: 3 ng ($1 : 8 \cdot 10^6$).
Blindversuch: bisweilen positiv, bis ungefähr 1 ng.

Mit einigen Ionen wurden bisher keine guten Erfolge erhalten.

Hg^{+2} und Bi^{+3} wandern in essigsaurer Lösung nicht, wahrscheinlich infolge Hydrolyse; das Gleiche gilt für Be^{+2}, das neutrale Moleküle des basischen Acetates bildet. Wenn dagegen eine genügend konzentrierte mineralsaure Lösung verwendet wird, erhitzt sich das Papier so stark, dass es verkohlt.

Al^{+3} konnte nicht empfindlich nachgewiesen werden, wegen des grossen Blindwertes von ungefähr 100 ng. Cu^{+2} empfand dieselbe Schwierigkeit, überdies schwankte der Blindwert stark.

Ba^{+2} wandert zwar nach der Kathode, der Nachweis mit Rhodizonsäure war aber mit 100 ng schon zweifelhaft; auch wurde in einem Chromatogramm eine positive Blindreaktion erhalten, vielleicht durch einen Ca-Gehalt des Papieres verursacht, oder durch Cu oder Fe.

Es ist einleuchtend, dass bei Empfindlichkeiten wie sie mit der hier beschriebenen Methode erreicht werden können, die Verunreinigungen des Papieres, der Reagenzien und des Wassers entsprechende Aufmerksamkeit erfordern. Aus diesem Grunde ist es auch notwendig, möglichst selektive Nachweisreaktionen zu wählen.

Für Zn^{+2} und La^{+3}, die wohl nach der Kathode wandern, haben wir nicht genügend empfindliche selektive Reagenzien finden können. Für den Nachweis im Papier beschränkt sich die Wahl auf Farbreaktionen, und diese eignen sich nicht alle zur Durchführung auf Papier.

MÖGLICHKEIT DER ANWENDUNG AUF PAPIERCHROMATOGRAMME

Zur Prüfung des Nutzens der beschriebenen Methode für Papierchromatogramme dienten einige Versuche mit den Kationen von Ni, Co und Mn. 25 µl der die Chloride enthaltenden Versuchslösung wurden auf den Streifen (Whatman Nr 1) gebracht und nach Trocknen wurde das Chromatogramm nach der Methode von Burstall *et al.*[19], jedoch mit steigender mobiler Phase (Aceton-Salzsäure-Wasser), hergestellt; die vordere Flüssigkeitsfront wanderte ungefähr 20 cm, die Zeitdauer war 3 Stunden.

An den mit Hilfe der bekannten R_F der Kationen berechneten Stellen (wenn nötig können die Werte gleichzeitig in einem Parallelversuche mit grösseren Konzentrationen bestimmt werden) wurden dann drei spitze Kathoden aufgestellt und die Kationen in der oben beschriebenen Weise zusammengezogen.

In einem Vorversuche war geprüft worden wie Ionen aus mehreren Flecken wandern, wenn zwei Elektroden gleichzeitig auf dem Papier stehen.

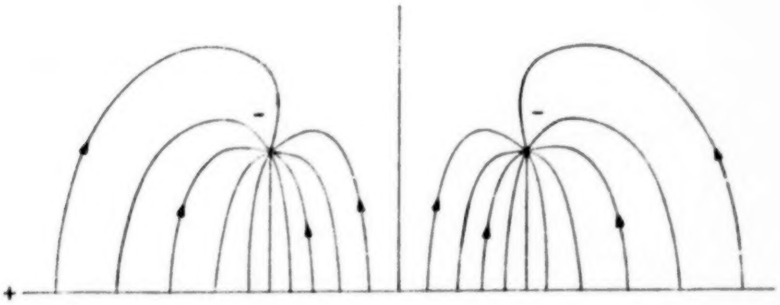

Abb. 1. Bahnen von Kationen bei Anwendung von zwei Kathoden.

Abb. 1 zeigt die Bahnen der Ionen. Das Bild wurde erhalten mittels eines Versuches von einigen Minuten mit einem quadratischen Gitter von sehr kleinen Tüpfelchen einer Nickellösung. Die Wirkungssphären der beiden Elektroden sind deutlich durch die Mittelsenkrechte zu ihrer Verbindungslinie voneinander getrennt.

Abb. 2 zeigt die Aufstellung des Versuches mit dem Chromatogramm. Zur Verminderung des Austrocknens wird neben den Apparat ein nasser Streifen Papier gelegt und das Ganze mit einer Kappe, z.B. aus einem durchsichtigen Kunststoffe, bedeckt.

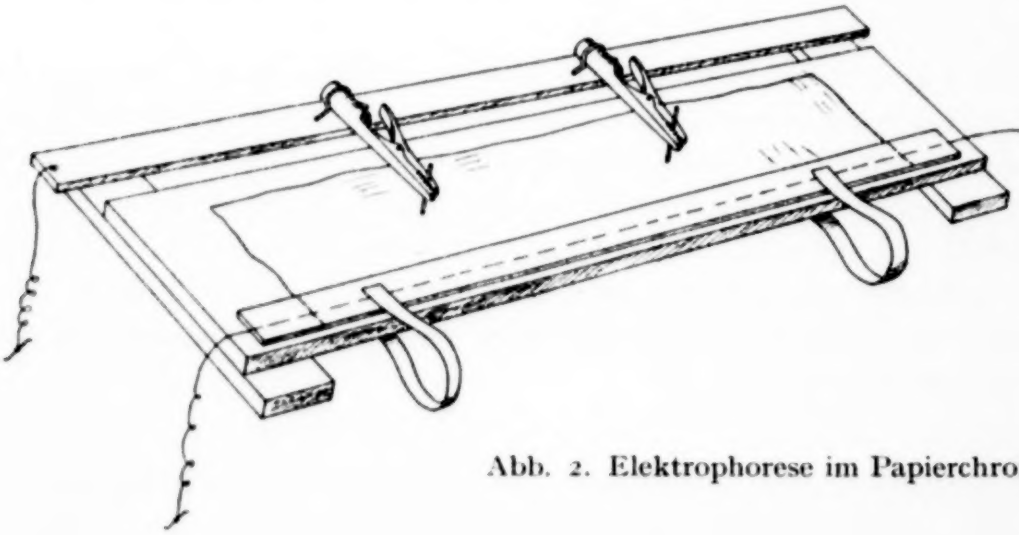

Abb. 2. Elektrophorese im Papierchromatogramm.

Es zeigte sich dass Ni^{+2}, Co^{+2} und Mn^{+2}, zusammen in Lösung, im Chromatogramm wiedergefunden wurden wenn Mengen von respektive 1, 2 und 3 ng gegeben waren. Ohne das elektrophoretische Zusammenziehen der Ionen wurden, ebenfalls mit 25 μl

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Versuchslösung, für die Nachweisbarkeitsgrenzen Werte von respektive 300, 100 und 200 ng gefunden. Durch das Zusammenziehen wurde die Empfindlichkeit für diese Ionen also etwa hundertfach verbessert.

Um einen Eindruck davon zu bekommen, in welchem Masstabe diese Ionen noch als Mikrokomponenten neben einer grösseren Menge eines der andern Ionen nachweisbar sind, wurden drei Chromatogramme hergestellt mit je 25 μl Lösung, die jedesmal eins der Ionen in einer Menge von 500 μg, die andern zwei in Mengen von 10 ng enthielten. Das Mengenverhältnis war also 1 : 50.000. Nach Konzentrieren an den Kathoden wurden die 10 ng deutlich nachgewiesen. Die Nachweisbarkeitsgrenzen lagen niedriger, wurden aber nicht genau aufgesucht. Einer Störung unterlag nur das Mn neben Überschuss von Co; die Spuren des letzteren, die, wie es wohl bei allen Ionen der Fall sein dürfte, auf dem zurückgelegten Wege zurückgeblieben sind, reagieren positiv mit dem Manganreagens (Luftoxydation, danach essigsaures Tolidin); das Mn konnte also nicht nachgewiesen werden.

Das Zusammenziehen der Ionen kann auch dem Chromatographieren vorangehen. Wegen der Kleinheit des Fleckens brauchen die verschiedenen Ionen dann nur einen relativ kurzen Weg zur völligen Trennung. Es resultiert also ein merklicher Zeitgewinn.

Der Tüpfel wurde in einer Entfernung von 2 cm vom Ende eines Streifens von 15 cm Länge und 2 cm Breite aufgebracht. Die Elektroden wurden wie in Abb. 3 angegeben aufgestellt, weil in einem so schmalen Streifen sich jenseits der Kathode kaum Kraftlinien vorfinden.

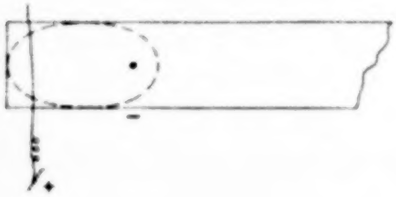

Abb. 3. Aufstellung der Elektroden wenn die Elektrophorese vorangeht.

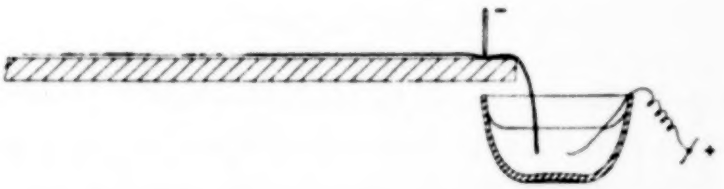

Abb. 4. Elektrophorese mit grösserer Menge Lösung.

Zur Überführung der gebildeten unlöslichen Verbindungen in Chloride wurde das Papier nach dem Trocknen einige Minuten lang der Einwirkung von HCl-Dampf ausgesetzt (Zylinderglas mit ein weinig NaCl und H_2SO_4), dann wurde während 15 Minuten chromatographiert. Das getrocknete Chromatogramm wurde an den richtigen Stellen (R_F) mit den erforderlichen Reagenzien besprüht, wobei jedesmal der Rest des Streifens mittels einer Papiermaske geschützt wurde.

Bei Verwendung von 25 μl Versuchslösung wurden in dieser Weise 2 ng Ni, 4 ng Co und 5 ng Mn nebeneinander gerade zurückgefunden.

Verunreinigungen des Papieres stören bei dieser Arbeitsweise nicht leicht, weil sie im allgemeinen andere R_F-Werte haben als das Ion auf das an einer bestimmten Stelle reagiert wird.

Grössere Flüssigkeitsmengen können nach der beschriebenen Methodik behandelt werden mit der einfachen Aufstellung, die in Abb. 4 skizziert ist.

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Die essigsaure Lösung, z.B. 1 ml, befindet sich in einem Schälchen oder Tiegel und wandert in den Papierstreifen, der auf einer Unterlage aus Perspex liegt. Die Lösung geht an der Elektrode vorüber, wo die Ionen gesammelt werden. Nachdem die Lösung völlig aufgesogen ist, wird das Papier getrocknet, wie oben angegeben mit HCl-Dampf behandelt und das Chromatogramm gemacht.

Mit dieser Arbeitsweise wurden Mengen von 10 ng Ni, Co und Mn nebeneinander in 1 ml Lösung (Konzentration 1 : 10^8) deutlich im Chromatogramm zurückgefunden.

Noch kleinere Konzentrationen könnten gewiss nachgewiesen werden, wenn grössere Mengen Lösung verarbeitet würden. Die Flüssigkeit könnte dann am andern Ende des Papierstreifens abtropfen.

Ob in dieser Weise die Ionen quantitativ an der Elektrode eingefangen werden, wird ausser von der gewählten Spannung auch von der örtlichen Breite des Papierstreifens abhängen. Wegen der orientierenden Art dieser Untersuchung haben wir diese Einzelheiten nicht weiter ausgearbeitet.

Vorläufige Versuche zeigten, dass auch Aminosäuren sich in der beschriebenen Weise konzentrieren lassen. Weil das Papier proteinartige Stoffe enthält, die mit dem gebräuchlichen Reagens Ninhydrin reagieren, war der Erfolg noch nicht gross. Immerhin wurden Hinweise darauf erhalten, dass die obige Methodik auch auf die genannten Verbindungen anwendbar sein dürfte.

Zusammenfassend lässt sich sagen, dass das Konzentrieren von Ionen mittels Elektrophorese die Möglichkeit bietet die Nachweisbarkeitsgrenzen weitgehend zu erniedrigen, meistens sogar um 1 bis 2 Grössenordnungen, bisweilen noch etwas weiter. Entscheidende Faktoren sind:

1. Die Wahl selektiver, möglichst empfindlicher Nachweisreaktionen, die sich zur Durchführung auf Papier eignen.
2. Reinheit von Papier und Reagenzien.
3. Elektrolytarme Lösung.

Die günstigsten Arbeitsbedingungen und die wirksamen Störungen müssen für jeden Fall gesondert aufgesucht werden.

Für stark hydrolysierende Ionen wurde noch keine erfolgreiche Arbeitsweise gefunden.

Der wichtigste Nutzen der beschriebenen Methode dürfte in der Anwendung auf Papierchromatogramme liegen, wo sich die Möglichkeit ergibt, Mikrokomponenten bis zu ziemlich niedrigen Konzentrationsgrenzen, auch neben Makrokomponenten, aufzufinden. Diese Arbeitsweise könnte also in der Spurensuche nützlich sein.

ZUSAMMENFASSUNG

Mittels Elektrophorese lassen sich viele Ionen in Papier um eine spitze Elektrode herum konzentrieren. Dadurch werden die Empfindlichkeiten ihrer Nachweisreaktionen erheblich verbessert. In 25 µl Lösung liegen die Empfindlichkeiten für die Kationen von Cd, Co, Cr, Mn, Ni, Pb, Tl^{I}, U^{VI}, Fe^{III} und Ag und für die Anionen von Au^{III}, B, Br^{-I}, J^{-I}, Mo^{VI} und V^{V} bei Konzenrationen von 1 : $2.5 \cdot 10^7$ bis 1 : $2.5 \cdot 10^5$.

In Papierchromatogrammen konnte weniger als 5 ng der Ionen Mn^{+2}, Ni^{+2} und Co^{+2} neben 0.5 mg eines der andern zwei nachgewiesen werden, mit Ausnahme von Mn neben Co.

Wenn die Elektrophorese vorher durchgeführt wird, dauert das Chromatographieren nur sehr kurze Zeit.

Damit ergibt sich auch die Möglichkeit, noch kleinere Konzentrationen in grösseren Volumina nachzuweisen.

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SUMMARY

By means of electrophoresis many ions may be concentrated around a pointed electrode. In this way the sensitivity of their spot tests may be improved considerably. With the kations of Cd, Co, Cr, Mn, Ni, Pb, Tl^{I}, U^{VI}, Fe^{III} and Ag and the anions of Au^{III}, B, Br^{-I}, J^{-I}, Mo^{VI} and V^{V} sensitivities between $1:2.5 \cdot 10^{7}$ and $1:2.5 \cdot 10^{5}$ were found when 25 µl of solution were used.

In paper chromatograms less than 5 ng of each of the ions Mn^{+2}, Ni^{+2} and Co^{+2} could be detected in presence of 0.5 mg of any of the other two, with the exception of Mn in presence of Co.

If the electrophoresis preceeds the chromatographing, the latter needs only a very short time.

In that way it becomes possible to detect even smaller concentrations in a larger volume of solution.

RÉSUMÉ

Plusieurs ions peuvent être concentrés sur papier-filtre, autour d'une électrode pointue, par électrophorèse. La sensibilité de leurs stilliréactions peut ainsi être considérablement améliorée. Pour les cations de Ag, Cd, Co, Cr, Fe, Mn, Ni, Pb, Tl^{I}, U^{V} et pour les anions de Au^{III}, B, Br^{-I}, I^{-I}, Mo^{VI} et V^{V}, en utilisant 25 µl de solution, on arrive à des sensibilités allant de $1:2.5 \cdot 10^{7}$ à $1:2.5 \cdot 10^{5}$. On peut déceler sur les chromatogrammes moins de 5 ng de Mn^{II}, Ni^{II} et Co^{II} en présence de 0.5 mg de l'un des deux autres, à l'exception du manganèse en présence de cobalt. Si l'électrophorèse est effectuée d'abord, la chromatographie se fait ensuite très rapidement. De cette manière, il est possible de déceler des quantités plus faibles dans des volumes de solution plus grands.

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RECTIFIED RADIO-FREQUENCY METHOD (R. Rf.) OF ZONE LOCATION FOR PAPER CHROMATOGRAPHY

by

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The author's conductimetric tube[1]* was described in the *Journal of Scientific Instruments* as long ago as 1945[2]. Various forms of this tube have been employed since then; these are depicted in Fig. 1 together with the dates of their publication.

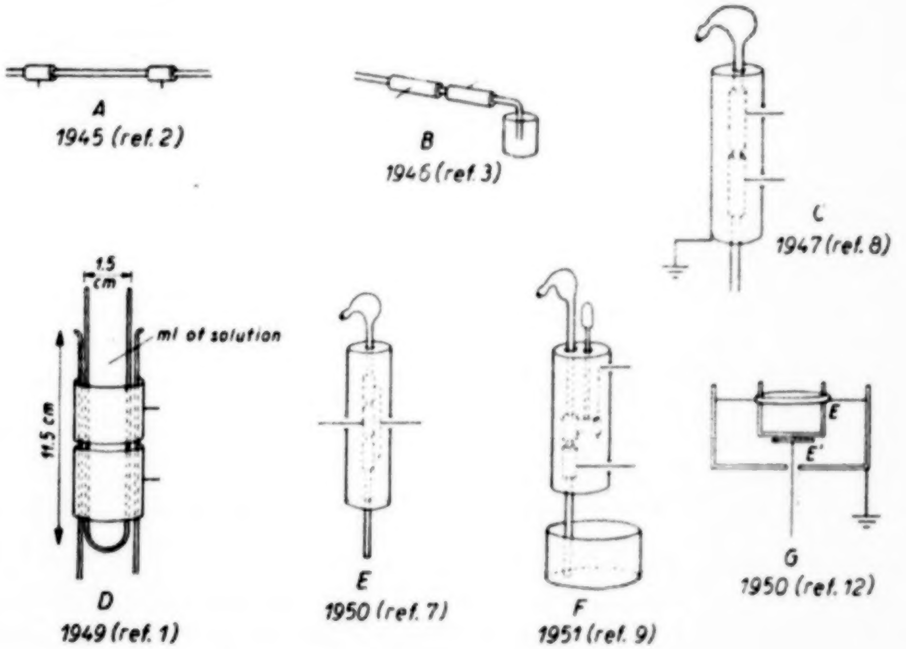

Fig. 1. Originally in 1936 when BLAKE first suggested and demonstrated the possibillity of applying radio-frequency to chemical analysis, he placed a glass beaker of solution on a metal plate connected to one of the oscillators of a heterodyne. The walls of the room constituted the second electrode; this was followed by the arrangement of electrodes seen in chronological order in this figure.

Shortly after WIDDINGTON in 1920[3] had shown that small physical measurements could be made by his heterodyne method, he author constructed a similar heterodyne arrangement, but it was not until 1936 that the applied this method to chemical analysis and demonstrated that a very small addition of any solute to a solution produced a measureable change of frequency[1]. In 1945, he introduced his Q-metric method (this measured variations in electrolytic conductance[2] and followed this in 1946 by his Rectified Radio-frequency method (R.Rf.)[4]. His work ever since has been on this latter principle.

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* The bibliography at the end of the paper supplies references to a number of papres by the author and others, in all of which the electrodes are located *outside* a tube containing the solution, and the radio-frequency energy is pulsed through the glass as a displacement current. Such a tube is termed by him a "conductimetric tube".

Interest in the heterodyne method was revived in 1950 by two papers which appeared in *Analytical Chemistry*[5], one by WEST, BURKHALTER AND BROUSSARD, and the other by BLAEDEL AND MALMSTAT. Each of these groups of workers used the principles which govern the conductimetric tube, *i.e.* they place their electrodes on the outside of a tube containing the solution and operate with displacement currents.

BLAEDEL AND MALMSTAT locate their electrodes, one underneath the container and the other around the outside (Fig. 1 G). It is a beautifully constructed little cell of which they give photographs and drawings in their paper.

More recently, MONAGHAM and his co-workers have also been working with the heterodyne method which they employ to detect the zones in a chromatographic column by frequency variations. Their outfit comprises two radio-frequency oscillators, a mixer, an audio-frequency oscillator and a cathode ray oscilloscope[6]. They attach two metal electrodes to the outsides of the glass tube containing the chromatographic column thus converting it into a "conductimetric tube". As ions are gradually adsorbed the zones or bands are located by alteration in the Lissajous figure on the screen of the oscilloscope.

In 1952[7] HALL published an electrical equivalent circuit to the conductimetric tube* (or cell as it was termed by him). He showed that it could be represented in terms of a variable resistance in series with a fixed capacitance possibly together with other fixed resistors and capacitors. Curves were given from which the resistance and capacitance of a very similar cell but fitted with submerged electrodes were evaluated. His work has clarified the theoretical considerations of the mode of operation of the conductimetric tube.

The rectified radio-frequency method of zone-location

The present paper presents a new variation of the condenser principle. Like the conductimetric tube the electrodes of the "zone locater" are separated from the conductive solution or solid conductive substance by a glass or other dielectric through which displacement currents operate. Fig. 2 is an explanatory diagram.

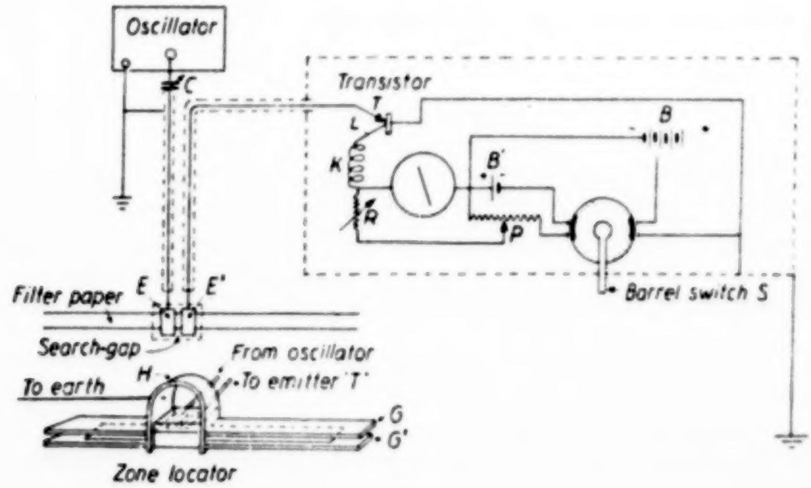

Fig. 2. These diagrams are self-explanatory, they indicate the operation of BLAKE's "zone-locater" for chromatography and a simple circuit in which a transistor performs the dual function of rectifier and amplifier.

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* The author, who originated the employment of external electrodes (*i.e.* insulated from the solution), in his writings terms all such arrangements "conductimetric tubes".

References p. 565.

PROCEDURE AND APPARATUS

A chromatograph on filter paper is made in the usual manner and is lightly moistened with the solvent which is sprayed on to it by means of an atomizer. It is then placed between two strips of glass G and G′.

Two metal foil electrodes E and E′ (Fig. 2) about 1 mm apart and firmly attached to an insulating block, are placed either over the top of glass G as in the sketch, or under the lower glass G′; H is a metal cover earthed to screen these from stray capacitance.

There are two alternative methods of operation:— the electrodes and their screen may be a fixture, and the glass strips containing the chromatograph can be slid along so that each zone in turn passes across the "search-gap"; alternatively the glasses may be a fixture and the "zone-locater" may be the movable member.

The electrical circuits are very simple and easy to construct. The radio-frequency current from an oscillator* is fed through a length of earth-screened cable to electrode E.

The energy pulses through the glass across the band of ions adsorbed on the filter paper and then through the glass again to the other electrode E′. Thence the *R_F*-pulsations are led through another length of screened cable to the emitter T of an n-type point contact transistor (or G.E.T.1.) where rectification and amplification take place. The operation and characteristics of the transistor have been described already by the author[8].

This circuit is practically self-explanatory. K is a Rf. choke. P and R are respectively the potentiometer and series resistance of the zero-shunt circuit[1], the opposing voltage for which is supplied by a battery B′.

Battery B supplies the negative voltage applied to the collector L. This governs the amount of amplification.

Both these batteries are switched on by means of the barrel switch S as indicated. Some idea of the response obtainable when an ionized zone passes across the search gap is indicated by the following test:— A band of an aqueous solution of *N*/400 KCl, approximately 8 mm, wide was painted by brush across a strip of filter paper. After it had dried, the whole strip was sprayed lightly with distilled water. The damp filter paper itself gave a small micro-ammeter deflection. This was set back to zero by zero-shunt adjustment.

As the band of KCl was slowly passed across the searchgap, the meter reading gradually rose from zero to 50 microamp. and then gradually fell back to zero. The maximum deflection was sharp and well defined.

With stronger concentrations much greater deflections are obtained and, in order to keep them within the range of the micro-ammeter scale either the coupling C or the amplification (or both) must be reduced.

The possibility of applying the R.Rf. method of zone location to column chromatography is now under investigation.

At the end of the REFERENCES auxiliary references[9] supply a list of papers having reference to the external location of electrodes.

SUMMARY

The employment of radio-frequencies for chemical analysis was suggested and commenced by the author in 1936. Brief mention is made of the gradual development of the "conductrimetric tube" with references to papers by him and other workers, and a new application of external electrodes and displacement currents to chromatography is presented. A circuit diagram is given in which both rectification and amplification are achieved by the use of a "Transistor".

RÉSUMÉ

L'emploi des radio-fréquences en chimie analytique a été proposé par l'auteur en 1936. Il relate brièvement le développement de la cellule conductimétrique en citant les références de ses travaux et de ceux d'autres chercheurs. Une nouvelle application des électrodes externes et des courants de déplacement à la chromatographie est présentée. Un diagramme du circuit est donné, dans lequel l'alimentation en courant rectifé et l'amplification sont obtenues par l'emploi d'un „transistor".

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* 1000 Kc/sec is recommended but much higher frequencies may be used if adequate screening be provided.

ZUSAMMENFASSUNG

Die Verwendung von Radiofrequenz in der analytischen Chemie hat der Autor im Jahre 1936 vorgeschlagen. Er erwähnt kurz die Entwicklung der konduktometrischen Zelle und zitiert die Referenzen seiner Arbeiten und die anderer Autoren. Es wird eine neue Anwendung der äussern Elektroden und der Wanderungsströme für die Chromatographie vorgeschlagen. Ein Stromdiagramm wird gegeben, in welchem ein rektifizierter Strom und die Amplifikation mittels eines „Transistors" erhalten werden.

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THE DETERMINATION OF SUB-MICROGRAM QUANTITIES OF SODIUM IN LITHIUM METAL BY RADIOACTIVATION

by

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I. INTRODUCTION

The most rapid and convenient method of determining sodium in small amounts is that of flame photometry, but the lowest concentration of sodium which can be detected in solution by a simple instrument is about 0.05 μg/ml and a 2 ml sample is required. The limit of detection is thus 0.1 μg of sodium and solutions must be fairly free of other elements whose characteristic spectral lines are excited in a flame, since the filter flame photometer does not have a sufficiently sharp cut-off to eliminate unwanted frequencies if the interfering elements are present in concentrations many times greater than the sodium. The permitted ratio of lithium to sodium is not greater than a few thousand and if more lithium is present, corrections become much too large.

INMAN, ROGERS AND FOURNIER[1] have shown the capabilities of a Perkin Elmer 52A flame photometer equipped with a monochromator. Using this more complex instrument the detection limit is 0.02 μg/ml sodium in solution and they successfully determined 10 p.p.m. of sodium in lithium metal without any need for chemical treatment other than solution of the metal and titration with sulfuric acid. The blanks for the dissolving process are constant (0.02 mg) and equal to about 10 p.p.m. sodium for the size of samples taken (1.5-3.5 g). The authors also show that 7000 p.p.m. lithium associated with 25 p.p.m. sodium causes a negative error of nine per cent in the concentration read for the latter element. It is not clear how large this suppression might become when the Li:Na ratio rises to more than a million to one, and in the concentrated solutions which would be required if the method of INMAN *et al.* were to be pressed to sodium concentrations ten or one hundredfold lower.

Other types of spectrochemical analysis suffer from similar problems of high blanks and also from the difficulties of preparing reliable standards with large quantities of lithium present to take account of enhancement or suppression effects on the sodium spectrum. Radioactivation, on the other hand, offers extremely high sensitivity, "blanks" are non-existent, contamination can be kept low by care in sampling, and pure sodium salts can be used as standards. The increase in time required is partially offset by the attractive lower limit of detection ($3 \cdot 10^{-10}$g sodium) associated with a 15 hour irradiation (flux $2 \cdot 10^{12}$ neutrons/cm^2/sec) and 80% chemical yield to give about 10 β counts/min above background.

The nuclear reactions used in the determination of sodium are

$$^{23}\text{Na} + n \rightarrow {}^{24}\text{Na} + \gamma \text{ (activation cross section 0.48 barns)}$$

$$\text{and } ^{24}\text{Na} \xrightarrow[\text{half life}]{\text{15 hour}} {}^{24}\text{Mg} + \beta + \gamma.$$

While the lithium under neutron irradiation produces tritium (12.1 yr half life), stable helium, and an active lithium isotope of very short half life, none of these interferes. Where sodium is present in large amounts, a short irradiation is possible followed by direct gamma counting[2,3]. In submicrogram quantities, the presence of other elements having a high cross-section makes this direct method unsatisfactory although SMALES AND SALMON[4] describe the use of a gamma spectrometer when the sodium content is greater than 10 μg, *i.e.* fairly high counting rates known are available. The unknown activity is always compared with the activity from a amount of sodium irradiated simultaneously with the sample.

Whenever the amount of sodium is only a few micrograms or less it is preferable to add sodium carrier to the irradiated material and perform whatever separations may be necessary to obtain a radiochemically pure sodium source for β-counting. LEDDICOTTE AND REYNOLDS[3] describe a system of several scavenges, an evaporation, and ignition followed by zinc uranyl acetate precipitation and 12% *n*-butanol-HCl reagent to convert the precipitate to NaCl, which was dried upon a tared filter paper, weighed and β-counted (sodium 5-15 p.p.m. in metal foils and aluminium). No information is given on the radiochemical purity of the final source by published decay curves. Experiments which we carried out with a simplified series of scavenges did not give satisfactory radiochemical purity with samples where the sodium content was below 1 p.p.m.

BROOKSBANK AND LEDDICOTTE[5] discuss the use of ion exchange for the separation of trace impurities and they define the conditions for the complete separation of the alkali metals on a column of Amberlite IR-1. LEDDICOTTE AND REYNOLDS[3] publish one result for sodium at the 70 p.p.m. level in mixed alkali metal carbonates using this scheme of activation and ion exchange. The severe disadvantages of the method are that over 13 hours is required for the ion exchange step and that the volume of the sodium fraction of the eluate is about 300 ml. (More recent work, not described, is said by the authors[5] to have reduced both time and volumes.)

Other authors have investigated the conditions under which excellent separations of the alkali metals are obtained on resin columns but the time required for elution is always exceedingly long and the volumes high, thus making the semiquantitative recovery of 20 mg of carrier sodium impossible unless further delay is admitted by introducing an evaporation step.

The present work is an effort to avoid these disadvantages and provide a method for the analysis of sodium in lithium which will make the utmost use of the sensitivity provided by radioactivation analysis without demanding unduly long chemical or physical procedures in order to prepare a radiochemically pure sodium source for β-counting.

The procedure described requires an overnight irradiation followed by chemical manipulation which includes an ion exchange separation on the semi-micro scale. The total time required for this radiochemical purification is about four hours for four samples and two standards. It may be used for sodium in lithium from 0.02

p.p.m. to 300,000 p.p.m. and greater without any alteration to the method (except for a reduction in the time of irradiation at the higher sodium levels).

II. (a) SAMPLING AND IRRADIATION

The irradiation phials were prepared in advance from 6 mm i.d. silica tubing (4 mm i.d. for standards). A length of the tubing was heated to redness in an oxygen-gas flame to destroy all grease. When cool it was carefully rinsed with pure water from a Deminrolite resin bed, drained and again heated to redness to drive off all moisture. Irradiation phials were then drawn and sealed off in pairs to be broken apart immediately before loading with the lithium metal samples. By sealing the tubes in pairs, two dozen or more could be made ready at one time without any danger of them acquiring internal sodium contamination from atmospheric dust while awaiting use. (Diagram, Fig. 1.)

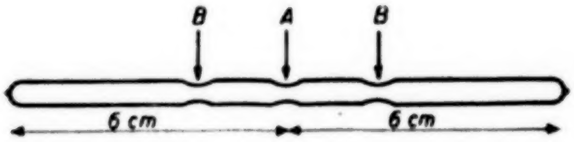

Fig. 1. A pair of silica irradiation phials. A and B are constrictions making it easier to open the phials for filling (A) and after irradiation (B) by scratching with a diamond at arrowed points.

In spite of the rapid dulling of freshly-cut lithium metal surfaces in air, all experiments directed towards sampling by cutting beneath the surface of an organic liquid such as ether showed that the surface contamination was markedly increased over sampling in air. Some slight advantage was gained by sampling from the bulk metal in the dry, still atmosphere of a glove box.

The simplest possible technique was eventually adopted. Small rectangular blocks (3 mm × 3 mm × 15 mm, 50-100 mg) of lithium are cut using a scrupulously clean scalpel and working upon a well cleaned aluminium sheet. The surfaces of the portions are repeatedly shaved away until a clean metallic surface is obtained which, however, clouds rapidly with the formation of a thin even film of blue-black lithium nitride. Analyses have shown that it is absolutely necessary to cut away all white Li_2O before irradiating the sample because the oxide layer has a very much higher sodium content than the bulk metal, indicative of atmospheric contamination during the corrosion process.

The irradiation phials are marked with an identification code, broken open, and weighed before sampling begins. As soon as a sample is cut, it is slipped into a phial ready for re-weighing and sealing. Four sample phials and two phials containing approximately 0.1 gram each of a standard solution of sodium (100 p.p.m.) are, after weighing, packed into an aluminium B.E.P.O. can which is irradiated overnight (12-15 hours) in a flux of $2 \cdot 10^{12}$ thermal neutrons/cm^2/sec and permitted to "cool" behind a shield for two hours before beginning the analysis.

A significant degree of self-screening may be expected owing to the high neutron absorption cross section of lithium (67 barns) consequently the larger the sample irradiated, the smaller will be the apparent sodium content found by radioactivation. In self-screening, the geometry of the sample will be of more importance than the weight and for a given mass the self-screening would be greater for a cube than for the elongated sample shape chosen. Because all samples were of similar geometrical proportions, the sample weight has been plotted against sodium content found (Fig. 2) for lithium containing 0.3% sodium. Contamination is not an important factor when the percentage of sodium is high and the spread of results may be taken as a measure of the precision of the radioactivation method for sodium in lithium subject to the variations in self-screening due to differing sample geometry.

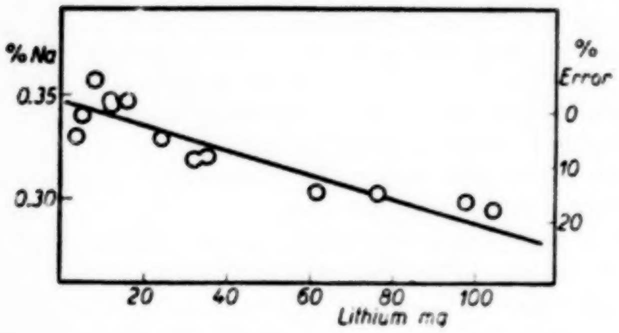

Fig. 2. Self-screening: the variation of apparent sodium content with sample weight.

The irradiation of samples weighing 50-100 mg introduces a mean negative error ranging from 10% to 20% due to self screening. Knowing the sample weight, an approximate correction for this error is possible using the graph of Fig. 2 and the right hand ordinate scale. At low levels of sodium ($<$ 1 p.p.m.) this effect is completely submerged by variations arising from superficial contamination of the lithium in the course of sampling from bulk. Nevertheless, the activities of the ^{24}Na sources reported in Table I have been increased by the appropriate correction for self-screening tabulated in the fifth column of the table.

II. (b) THE ANALYTICAL METHOD

On completion of the fifteen-hour neutron irradiation, the short-lived activity is permitted to decay for a few hours before the silica phials are opened. After the removal of superficial contamination by an acid rinse, the lithium slugs are dissolved in the presence of carrier sodium and a preliminary separation of the sodium is achieved by adding ethanol saturated with dry hydrogen chloride gas. Sodium is precipitated as sodium chloride while lithium remains in solution[6]. After centrifuging, the supernatant solution is discarded and the sodium chloride is dissolved and reprecipitated as sodium zinc uranyl acetate. Further treatment of the separated precipitate with ethanol-HCl reagent recovers the sodium as the solid chloride. This is dissolved in water, flowed on to a small ion exchange column and eluted with 1.1 N HCl. The sodium is recovered once again as chloride from the appropriate fraction of the eluate by addition of ethanol-HCl reagent. The precipitate is washed with absolute alcohol, then slurried and transferred to a weighed counting tray. The alcohol is evaporated off under an infra-red lamp before weighing again to permit calculation of the chemical yield. The β-activity of the ^{24}Na source is counted and compared with the activity of known standards, which were irradiated simultaneously and put through the same chemical treatment.

In Fig. 4, a composite ion-exchange elution curve is shown. All anionic activity passes through the column with the preliminary washings and sodium is the first cation to be eluted with the hydrochloric acid. The column does not separate the monovalent cations but retains divalent and trivalent ions. Separation of sodium from the bulk of the lithium and from potassium or other monovalent ions is completed by the chemical procedure.

Analytical procedure

Reagents

(1) *Zinc uranyl acetate reagent*: Place 77 g of uranyl acetate ($UO_2(C_2H_3O_2)_2 \cdot 2H_2O$) in a 1 litre beaker, add 13.3 ml of glacial acetic acid and 410 ml of water. Warm the solution to 70° C and stir to aid complete solution. Into a tared 600 ml beaker weigh 231 g of zinc acetate ($Zn(C_2H_3O_2)_2 \cdot 3H_2O$), add 6.6 ml of glacial acetic acid, 262 ml water, and warm with stirring to 70° C until all solids are dissolved. Pour the second solution into the first and allow to stand undisturbed for 24 hours at room temperature before filtering into a clean bottle for storage[7].

(2) *Ethanol-HCl reagent*: Place approximately 300 grams of sodium chloride in a 1 litre conical flask. Insert a cork carrying a gas delivery tube and equipped with a reservoir and stopcock for the controlled addition of concentrated sulphuric acid. Sufficient protection against the HCl gas may be afforded the cork by a heavy coat of collodion solution. The generating flask is placed on a hot plate at 50-60° C and the delivery tube led into a 500 ml bottle through a drilled polythene stopper. The delivery tube should be a half inch above the level of the absorbing liquid to allow for the volume increase which takes place. When ready to generate the HCl gas, 400 ml of absolute ethanol are poured into the receiving vessel and a few milliliters of concentrated sulphuric acid flowed on to the sodium chloride. The last 150-200 ml of acid (250 ml total) can be added fairly rapidly and the reaction left overnight to reach completion.

(3) *Standard sodium solution*: A standard sodium solution is required for simultaneous irradiation with the lithium samples, thus avoiding any need to know the pile flux with accuracy, the exact time of irradiation, or even self-absorption corrections for the final sources. A weighed aliquot of standard solution prepared from oven-dried AnalaR NaCl (Na^+, 100 p.p.m.) is passed through the entire analytical procedure from irradiation to final β-counting.

(4) *The ion exchange column* : Zeocarb 225 resin ($< 50\ \mu$ particles) is prepared by washing with several bed-volumes of $6N$ HCl. The resin is now in the hydrogen form and is rinsed with several bed-volumes of demineralized water and finally with ethanol after which it is spread out for air drying. Each column is loaded with 0.5 g of the prepared resin, slurried with water.

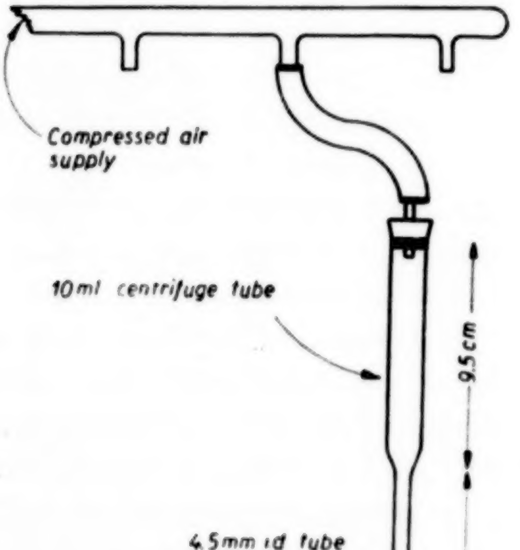

Fig. 3. The ion-exchange column.

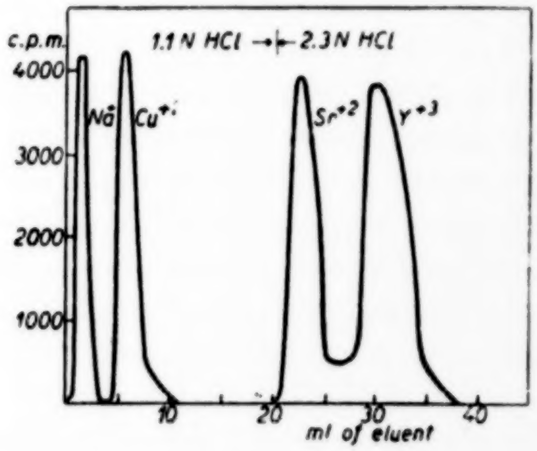

Fig. 4. The elution curve of four cations, using two eluents.

The glass column is made by sealing a 10 cm length of 4.5 mm i.d. glass tubing to the bottom of a calibrated 10 ml pyrex centrifuge tube as shown in Fig. 3. The hydrostatic head is insufficient to provide a reasonable flow rate (0.25 ml eluent/min.) so the reservoir is connected by flexible tubing to a compressed air manifold. The air pressure comes from the laboratory supply via a reducing valve (10 lbs/in^2) and a needle valve. The connection between the needle valve and the glass manifold has a small air leak in the form of a bunsen valve to stabilize the pressure applied to the column reservoirs through the six outlets of the manifold. An adequate control of the flow rate from 0.1 ml/min upwards is possible by manipulation of the needle valve. Total pressure required varies only slightly from column to column and is in the vicinity of 5 cm of mercury.

Procedure

Cut four samples, 50-100 mg each, of lithium metal (3 mm × 3 mm × 15 mm approx.) and weigh in prepared silica irradiation phials. Record the sample weight and seal the phials. Weigh accurately about 0.1 grams of 100 p.p.m. standard sodium solution into each of two small silica phials and seal off. Irradiate for fifteen hours in a neutron flux of 2×10^{12} neutrons/cm^2/sec for ten parts per million or less of sodium in lithium. Decrease the irradiation time in inverse proportion to sodium contents over ten parts per million. Allow two or three hours cooling for short-lived activity to decay.

Break open the phials containing the metal samples and drop the slugs into 10 ml absolute ethanol, 0.25 ml 1.2*N* HCl and two drops of methyl red indicator in a 25 ml beaker. Remove the slug and rinse quickly with absolute ethanol when the solution becomes alkaline. Discard the solution which contains any superficial contamination. Transfer the metal immediately to a 40 ml centrifuge tube containing 10 ml absolute ethanol, 2 ml Na carrier solution (25 mg NaCl/ml) and two drops of methyl red indicator. To this solution is added, dropwise at first, 2 ml of concentrated HCl in order to maintain an acid solution but avoid too vigorous evolution of hydrogen.

Break open the phials containing the standards and rinse the contents into a 100 ml volumetric flask using a dropping pipette to extract the active solution and rinse the phial with a wash solution containing 50 mg NaCl (2 ml of 25 mg NaCl/ml carrier solution). Make up to volume, mix well, and withdraw 1 ml, placing this in a 40 ml centrifuge tube with 10 ml absolute ethanol, 2 ml sodium carrier solution, and 2 ml concentrated HCl.

Add 15 ml of ethanol-HCl reagent to the solutions in all six 40 ml centrifuge tubes. Chill in an ice-bath for a quarter of an hour, centrifuge, discard the supernate and wash the precipitated sodium chloride twice with 2-3 ml absolute ethanol. Use a stirring-rod to disperse the precipitate. Discard all washings. Dissolve the NaCl in 0.5 ml of water, heating if necessary to speed solution. Add 25 ml of zinc uranyl acetate reagent to reprecipitate the sodium. Digest at room temperature for 15-20 minutes with occasional stirring. Centrifuge, and wash the precipitate thoroughly with two 10 ml portions of methylated spirits. Discard all supernates. To the sodium zinc uranyl acetate add 15 ml ethanol-HCl reagent. Centrifuge and wash the sodium chloride twice with 5 ml portions of absolute ethanol. Discard all supernates.

Dissolve the precipitate in 0.5 ml of water and transfer to the top of a prepared column of Zeocarb 225 (see above) using a small dropping pipette. Rinse the centrifuge tube with a further 0.5 ml of water and add the washing water to the column. Adjust the pressure of compressed air so that the flow rate of solution through the column is 0.25 ml/min. When the active sodium solution is absorbed on the column, wash the resin with an additional 1 ml of water. Commence elution (con. HCl 1:10) when the level of washing water falls to the top of the resin bed. Discard all column washings and the first millilitre after elution begins. Collect the following 2 ml fraction, containing the sodium, in a 40 ml centrifuge tube.

Add 15 ml ethanol-HCl reagent to the sodium fraction of the eluent. Chill the centrifuge tube and its contents in an ice-bath for 10-15 minutes. Centrifuge and wash twice with 3 ml portions of absolute ethanol using a stirring rod to break up the precipitate. Slurry the sodium chloride in 0.5 ml of absolute alcohol and plate out on a weighed counting tray. Dry the slurries under an infrared lamp, weigh, and β-count for an appropriate period.

The measured activity for the standards is corrected for chemical yield making allowance for the additional 1% of carrier present. The activity of the samples is similarly corrected and further adjustments made for the effects of selfscreening, using the graph in Fig. 2. If counting has taken more than 5 minutes each, correction for decay (^{24}Na half-life, 15 hours; decay 4.5% per hour)may be made to later counts taking the time of the first count as zero time.

If the corrected β-activity for a sample is A, the fractional chemical yield, Y, and F is an average factor calculated from the two standards,

$$F = \mu\text{g Na/count/min}$$

then we have the sodium content of the lithium expressed as

$$\text{p.p.m. Na} = \frac{A \times F}{Y(W-2)} \times 10^3$$

where $(W-2)$ is the weight of the lithium sample in milligrams corrected for the loss of 2 mg in the first acid wash used to reduce superficial contamination.

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III. RESULTS AND CONCLUSIONS

The results of three sets of replicate analyses on two different samples of lithium metal are shown in Table I.

TABLE I

Sample	*Counts/min corrected for background*	*Carrier recovery*	*Decay factor*	*Self-screening corrections*	*Corrected Counts/min*	*Micro-grams of sodium*	*Milligrams of lithium*	*p.p.m. sodium in lithium*
8-47	75	86.7%	—	+15%	98	0.00248	80.2	0.031
48	67	82.6%	0.992	+16%	95	0.00240	85.0	0.028
49	45	82.4%	0.985	+13%	63	0.00159	64.2	0.025
50	66	80.1%	0.976	+12%	94	0.00238	61.6	0.039
Std 23	3 187	81.9%	0.968	—	4 020	0.0997	$0.248 \cdot 10^{-4}$ μg Na/count/min	
Std 24	3 353	83.7%	0.964	—	4 160	0.107	$0.258 \cdot 10^{-4}$,, ,, ,, ,,	
							Av. $0.253 \cdot 10^{-4}$,, ,, ,, ,,	
					Av. Sodium Content: 0.031 ± 0.004 p.p.m.			
9-9	391	84.2%	0.997	+13%	526	0.0678	76.0	0.89
10	398	84.6%	0.993	+14%	539	0.0695	80.0	0.87
11	289	86.0%	0.990	+ 9%	370	0.0477	52.9	0.90
12	285	81.8%	0.987	+10%	388	0.0501	57.4	0.87
Std 17	1023	85.6%	—	—	1198	0.153	$1.28 \cdot 10^{-4}$ μg Na/count/min	
Std 18	838	85.0%	0.983	—	1002	0.131	$1.30 \cdot 10^{-4}$,, ,, ,, ,,	
							Av. $1.29 \cdot 10^{-4}$,, ,, ,, ,,	
					Av. Sodium Content: 0.88 ± 0.01 p.p.m.			
10-1	1025	79.5%	0.902	+18%	1690	0.117	95.5	1.22
-2	1155	79.0%	—	+17%	1710	0.119	91.9	1.30
-3	1120	74.8%	0.985	+17%	1780	0.124	90.1	1.38
-4	1125	78.5%	0.970	+19%	1760	0.122	99.9	1.22
Std 21	1110	76.0%	0.955	—	1531	0.104	$0.68 \cdot 10^{-4}$ μg Na/count/min	
Std 22	1090	84.4%	0.940	—	1376	0.098	$0.71 \cdot 10^{-4}$,, ,, ,, ,,	
							Av. $0.695 \cdot 10^{-4}$,, ,, ,, ,,	
					Av. Sodium Content: 1.28 ± 0.06 p.p.m.			

The importance of removing all traces of lithium oxide from the surface was shown by a further series of four replicate analyses where significant oxide contamination was allowed to remain. The sodium content then ranged from 0.098 to 0.216 p.p.m. (average 0.15 p.p.m.) compared with 0.03 p.p.m. for careful sampling.

The radiochemical purity of all sources was checked by observing their decay down to a few counts per minute above background. The decays for sample 8 are plotted in the graph of Fig. 5.

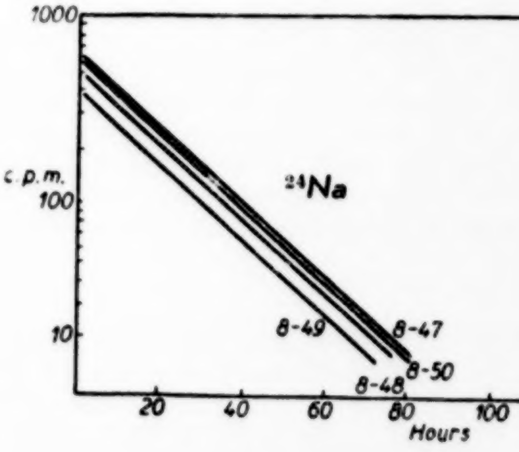

Fig. 5. Four typical decay curves.

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SUMMARY

This report describes an analytical procedure for sodium in lithium metal. As little as $2 \cdot 10^{-9}$ g of sodium (0.02 p.p.m.) is readily determined by neutron activation of the sample followed by separations to isolate radiochemically pure sodium-24.

RÉSUMÉ

Une méthode est décrite pour le dosage du sodium dans le lithium métallique. On peut doser rapidement jusqu'à $2 \cdot 10^{-9}$ g de sodium (0.02 p.p.m.) par activation de l'échantillon au moyen de neutrons, puis séparation du sodium-24 radiochimiquement pur.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben, um Natrium in metallischem Lithium zu bestimmen. Man kann schnell bis zu $2 \cdot 10^{-9}$ g Natrium (0.02 p.p.m.) bestimmen, nach einer Aktivation der Substanz mit Neutronen und anschliessender Abtrennung des radiochemisch reinen Natrium-24.

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DETERMINATION OF TRACE QUANTITIES OF BISMUTH IN LEAD AND COPPER

by

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INTRODUCTION

During World War II, extensive corrosion of the lead equipment used in the manufacture of smokeless powder was experienced at many ordnance works. The corrosion was most evident in the sheet lead lining and steam coils of the ether still pots. One of the factors which seemed to be responsible for this trouble was the presence of very small amounts of bismuth in the lead. Little published information on this point is available[9,12]. However, specifications were set up by the ordnance plants for an exceedingly low tolerance of bismuth in the lead. Improved methods were needed for the determination at the low levels specified.

Similarly to lead, copper has been found to show defects as a consequence of the presence of small amounts of bismuth. Quantities of the order of 0.001% can cause embrittlement[18,27,33] in working the metal at temperatures between 450 and 460° C. The situation as regards the need for analytical procedures was like that for lead.

For the determination of traces of bismuth in lead numerous spectrographic procedures have been employed[2,21,22]. D. M. SMITH[30] reports quantities of this element below 0.0005% are not detectable by spark excitation of metallic electrodes and quantitative spectrographic determinations of amounts of this order by any method of excitation without preliminary concentration have not been satisfactory. Experiments in this laboratory[8] have confirmed this conclusion. This state of affairs led to a comprehensive survey of existing methods for trace amounts of bismuth. Almost every conceivable technique—spectrographic, gravimetric, volumetric, nephelometric, electrolytic, radiometric, catalytic, chromatographic, ion exchange and colorimetric—has been employed or suggested. As a result of this survey[8] the colorimetric iodide procedure, applied after a preliminary removal of most of the lead seemed most promising for this phase of the problem. The most favorable reagents for the colorimetric determination of traces of bismuth are dithizone, thiourea, thiocyanate and iodide. A consideration of each indicates that the problem of interferences is of major concern. Dithizone, although extremely sensitive, reacts with a great many metal ions, some of which can be rendered innocuous by use of complexing agents. Unfortunately, lead reacts under the same conditions as bismuth and must be carefully removed. For this reason dithizone was not considered practicable for the type of sample involved. Thiourea is highly specific for bismuth but is of lower sensitivity. Thiocyanate reacts with bismuth similarly to iodide. A large excess of reagent is necessary and the resulting color is more unstable. The iodide method is less subject to objections. Lead interference is less serious than in the dithizone method, for it is only necessary to reduce the lead concentration to the level at which lead iodide does not interfere. Of the various ions liable to cause interference with the iodide procedure, antimony is most probable. It must be present in only moderate amounts. The object of the present investigation was to extend the sensitivity of this colorimetric method to the useful determination of bismuth in a lower concentration range.

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The iodide method is based upon the fact that excess iodide in acid solution forms a yellow iodobismuthous ion, which in the visible range, has an absorption maximum near 460 mμ. SANDELL[28] presents a discussion of certain aspects of the procedure. The color intensity of the bismuth compound increases when potassium iodide in amounts up to 1% is added, but then remains practically constant[33]. Beer's law is followed and the color is stable for at least ten days[32]. ROBINSON[26] employed the procedure to determine 0.0005% or more of bismuth in lead after taking a 20 g sample and making a preliminary separation of the lead as the chloride. The oxychloride of bismuth was gathered by a coprecipitation with ferric hydroxide. The presence of iron has been shown to be undesirable, in that it increases the probability of formation of iodine and of a contribution of its color to that of the bismuth salt. Hence, some other method of gathering the precipitate is desired. Since the oxygen of the air and other oxidants may cause the formation of iodine, some reducing agent must always be present to prevent it. Sulfurous acid has been proposed[32] but a high concentration must be avoided because of the formation of a yellow iodosulfinic acid. Hypophosphorous acid has also been recommended, but it is reported to act very slowly at room temperature. ROBINSON heated the solutions to 70° C to insure complete reduction of iodine. A mixture of phosphorous acid and sulfurous acid is not permissible because of the formation of finely divided sulfur.

Because of contradictory findings or lack of complete information in the literature, the initial experiments in the present work were devoted to a reexamination of the use of ferric hydroxide as a collecting agent and a further study of the reducing materials used for prevention of iodine interference. Attention was given to the absorption of the bismuth iodo compound in both the visible and ultraviolet regions of the spectrum, not only in aqueous solutions but also in organic solvents.

In the separation of the major portion of the lead from the bismuth, the effects of pH and other factors associated with the collection of the bismuth upon silica materials were studied along with the conditions for its elution and estimation as the iodide.

Attention was given to the possible interference of antimony with the final bismuth estimation.

In the case of the copper samples experiments were carried out in which the bismuth was collected from an ammoniacal solution.

References pp. 586/587.

STUDY OF THE COLORIMETRIC IODIDE METHOD FOR BISMUTH DETERMINATION

Apparatus and materials

Spectrophotometer, Beckman Model DU.

All chemicals were analytical reagent grade.

Bismuth standard solution containing 100 γ of bismuth per ml prepared by dissolving 0.115 g of bismuth oxide in 5 ml of 1:1 nitric acid and diluting to 1 liter with distilled water. Less concentrated standards were prepared by dilution of this solution.

Ferric iron solution containing 1 mg Fe^{+3}/ml prepared by dissolving 2.1 g of iron in nitric and sulfuric acids and diluting to 2 liters with water.

Sodium sulfite solutions. A 0.5% solution prepared by adding 1 g of the salt to water acidified with 0.8 ml of sulfuric acid and diluting to 200 ml. A 2.7% solution prepared by adding 2.7 g of the salt to water acidified with 1 ml of sulfuric acid and diluting to 100 ml. These solutions were freshly prepared.

Ascorbic acid, 1% in water, also freshly prepared.

Potassium iodide.

Hypophosphorous acid, 30% and 50%.

Antimony solutions. Concentrations of 1 mg/25 ml, 4 mg/25 ml, and 20 mg/100 ml prepared by dissolving the required amount of metallic antimony in concentrated sulfuric acid and diluting to volume to give a final sulfuric acid concentration of 1:40 - equivalent to that found in the solutions used in the bismuth determination.

Organic solvents. Amyl alcohol, ethyl acetate, amyl acetate and diethyl ketone.

Determination in aqueous medium

Determination of the absorbance of the yellow iodobismuthite color at 460 mμ is subject to interference due to the presence of iodine formed by oxidation of iodide ion which must be present in excess. Various reductants have been recommended to prevent this interference, and the efficiencies of sodium sulfite and hypophosphorous acid were tested using ferric iron as an oxidizer. Samples containing 0, 100, 200, 300, and 400 γ of bismuth in 50 ml of 1:20 sulfuric acid were treated with 5 mg of ferric iron. To one series were added 13.4 ml of 0.5% sodium sulfite and to the other 5 ml of 30% hypophosphorous acid. The solutions were diluted to 100 ml after the addition of 1.5 g of potassium iodide, and the absorbances of the solutions *vs.* water were determined with a Beckman DU spectrophotometer in 1 cm cells at 460 mμ. Comparison of the absorbance values after correction for the blanks showed no differences between the two series for any given bismuth concentration. However, the sulfite blank had an absorbance of 0.007 while the hypophosphorous acid blank was only 0.003. The higher sulfite blank may result from the formation of the yellow iodosulfinic acid.

The effect of heating on the hypophosphorous acid series was investigated since the action of hypophosphorous acid is reported to be slower than sulfite and ROBINSON recommended this procedure to insure rapid reduction of iodine. However, when the above samples were heated to 70° and then cooled to room temperature for photometering, no changes were observed.

Because sulfite gave higher blank absorbance values and was subject to the problem of forming a colored reaction product with iodide it was rejected as the reducer and hypophosphorous acid was adopted in preference. The samples were not heated prior to measurement of the absorbance, and no iodine was ever detected by the starch test or by ultraviolet absorption in any of the final solutions sampled during the course of the experimental work. Thus, the interference due to iodine formation can be eliminated by the use of hypophosphorous acid.

A calibration curve was prepared by adding 100 to 400 γ of bismuth to 50 ml of 1:20 sulfuric acid. Five ml of 30% hypophosphorous acid and 1.5 g of potassium iodide were then added, and the solution was diluted to 100 ml with distilled water. The absorbance values were measured at 460 mμ in 1 cm cells and were identical with those of the solutions above containing iron (Table I).

Improvement in the determinable value was obtained by reducing the final volume to 25 ml and using 5 cm absorption cells. The reagent concentrations were reduced proportionally. To 12.5 ml of 1:20 sulfuric acid, 0, 10, 20, 50, 70, and 100 γ of bismuth were added followed by 1 ml of 30% hypophosphorous acid and 0.375 g of potassium iodide. The solutions were diluted to 25 ml, and the absorbance values were determined in 5 cm cells at 460 mμ.

Conformance to the Beer-Lambert Law in the use of both 1 cm and 5 cm cells is indicated by the data in Table I. The reference cell contained water. The reagent blanks have been subtracted from the other absorbances to give the values tabulated.

Antimony, like bismuth, forms a colored iodide complex, but a very large excess of iodide is required. The color is almost nil at a potassium iodide concentration of 1.5% which is used for bismuth. Evaluation of the color produced by antimony under the conditions described showed that 20 mg of antimony per 100 ml of solution were required to give the same absorbance as 20 γ of bismuth. In a 25 ml volume using 5 cm cells 1 mg of antimony showed no absorbance while 4 mg showed an absorbance of 0.074.

TABLE I

ABSORBANCE VALUES FOR BISMUTH IODIDE COMPLEX AT 460 mμ

Bismuth γ/100 ml	A 1 cm cells
0 (Blank)	0.003
100	0.045
200	0.092
300	0.138
400	0.183
γ/25 ml	5 cm cells
0 (Blank)	0.012
10	0.102
20	0.195
40	0.380
70	0.667
100	0.951

The ultraviolet absorption spectrum of the bismuth iodide complex was examined to determine whether an absorption region band more sensitive than that at 460 mμ might be used for bismuth estimation. A solution containing 300 γ of bismuth per 100 ml prepared as above, was examined in the 300-400 mμ region with the aid af a Cary Recording Spectrophotometer. Although the complex exhibited an absorption maximum at 336 mμ which was 2.5 times more intense than the visible absorption, it was not possible to obtain reproducible blanks. The observed absorbance at 336 mμ varied with time of standing, and the shapes of the ultraviolet curves were altered by heating (although the net absorbance was unchanged). This behavior was encountered with both sulfite and hypophosphorous acid reducers. These unfavorable factors indicate that use of the 336 mμ band for bismuth estimation would be subject to many sources of error and a high degree of uncertainty. In addition, extraneous materials would be much more liable to cause difficulty in the ultraviolet region. Not only for these reasons but also because it was felt that a 2.5-fold increase in sensitivity did not warrant the necessity for an ultraviolet instrument, the 336 mμ absorption region was not studied further.

Extraction with organic solvents

The yellow iodobismuthite can be extracted into organic solvents, and this technique was investigated to determine if greater sensitivity could be realized. HADDOCK[14] used a mixed solvent of amyl alcohol-ethyl acetate (3:1). However, the problem of iodine formation is much more important when the extraction technique is used since iodine shows visible absorption as well as ultraviolet absorption at 362 and 293 mμ in this solvent. The mixed reducing agent consisting of 5 ml of 1% ascorbic acid and 1 ml of 1% sodium sulfite recommended by GIACOMINO[13] was found to be satisfactory for the prevention of iodine formation during the extraction. One hundred γ of bismuth were extracted from 25 ml of 2*N* sulfuric acid containing 1 ml of 10% potassium iodide and the mixed reducer. Satisfactory, reproducible blanks and samples were obtained for measurement of the bismuth iodide complex absorbance at 460 mμ. However, as expected, measurements in the ultraviolet region were not satisfactory. One disadvantage of the extraction procedure is that the color is stable only 20 to 30 minutes. In addition, the absorption is stronger in in aqueous medium by a factor of almost 2. Neither diethyl ketone nor amyl acetate showed any advantage over amyl alcohol-ethyl acetate (3:1) as an extraction medium with regard to sensitivity.

Conclusion

Based on considerations of speed, convenience, accuracy, and sensitivity it is most satisfactory to measure the absorption of the bismuth iodide complex in the visible region at 460 mμ and to measure it in aqueous medium.

PROCEDURE FOR DETERMINATION OF TRACES OF BISMUTH IN LEAD

Apparatus and materials

All reagents of analytical reagent grade.
Spectrophotometer, Beckman Model DU.
pH meter (a Beckman Industrial Model was used).
Silica flour (Celite and Super Cel obtained from the Johns-Manville were used).
Gooch crucibles prepared with an asbestos mat (4 mm), a perforated disc, and a thin (3-5 mm) layer of silica flour.
Nitric and hydrochloric acids.
Ammonium acetate, 20%.
Sodium hydroxide.
Sulfuric acid, 1:20.
Hypophosphorous acid, 30%.
Potassium iodide.

Method

Dissolve 20 g of the sample in a mixture of 25 ml of nitric acid and 50 ml of water in a 400 ml beaker. Heat if necessary. Add 30 ml of hydrochloric acid to precipitate lead chloride and cool to 0-5° C in an ice bath. Filter off the lead chloride in a Buchner funnel (diameter 5.5 cm) using a double layer of Whatman No. 1 filter paper. Wash the precipitate with cold 1:1 hydrochloric acid 3 times. Return the filtrate and washings to the 400 ml beaker and add 20 ml of 20% ammonium acetate to the filtrate and neutralize by adding sodium hydroxide pellets. (If the reaction becomes too violent, cool in the ice bath). Cool the solution to room temperature and adjust the pH to 6.0-6.25 with a pH meter by adding sodium hydroxide or hydrochloric acid solution. Add 2.5 g of silica flour (if the sample contains 0.0005% or less bismuth 1 g can be added, and this makes mechanical handling somewhat simpler). Stir well. Allow the sample to stand for 1 hour, and agitate it intermittently during this period. Filter off the silica on a Gooch crucible prepared as above. Wash the collected silica 3 times with water. Elute the bismuth with 12.5 ml of hot 1:20 sulfuric acid. Add 8-9 ml of the acid and allow it to flow through the silica by gravity and then apply moderate suction. Add the remaining hot 1:20 sulfuric acid and allow it to flow through the silica by gravity. Finish the elution by applying suction and washing twice with a little water. A 50 ml filter flask is convenient for receiving the eluate. Add 1 ml of 30% hypophosphorous acid and 0.375 g of potassium iodide and dilute to 25 ml. If the solution is turbid, filter through a fine sintered glass filter. Determine the absorbance at 460 mμ and compare to bismuth standards treated to form the yellow iodobismuthite color in the same way. If less than 0.0005% bismuth is present the absorbance should be measured in a cell which is 5 cm long.

Discussion of method for bismuth in lead

The procedure given is essentially a modification of the one proposed by ROBINSON in which ferric hydroxide is used as the gathering agent.

References pp. 586/587.

A preliminary study of the use of silica as a collector indicated that the batch procedure was preferable to the use of a column because of greater simplicity and speed. It was found that both Celite and Super Cel silica materials were equally satisfactory and that a waiting period before filtration was desirable. It was also established that the presence of chloride ion is unnecessary for bismuth recovery and that pH control is necessary.

To study the effect of pH on bismuth recovery, 300 γ of bismuth were added to 300 ml of water and 5 ml of hydrochloric acid. The pH was adjusted with the aid of a pH meter by addition of sodium hydroxide solution, and the bismuth was recovered as indicated in the procedure except that a final volume of 100 ml was used for color development and the potassium iodide and hypophosphorous acid concentrations were adjusted accordingly. The bismuth recovery was calculated from the observed absorbance, and the results showing bismuth recovery as a function of pH are tabulated in Table II. At pH values much below 6 or about 11 the recovery will be low.

TABLE II

EFFECT OF PH ON BISMUTH RECOVERY FROM WATER SOLUTIONS CONTAINING HCl

pH	*A (obs)*	*% Bi Recovered*	*Average*
4	0.042	30	30
	0.040	29	
5	0.091	67	67
	0.092	67	
6	0.132	96	98
	0.136	99	
6.7	0.137	99	100
	0.138	100	
7	0.138	100	100
	0.136	99	
8	0.136	99	99
	0.137	99	
9	0.138	100	100
	0.138	100	
10	0.137	99	100
	0.138	100	
11	0.124	90	89
	0.120	87	
12	0.113	82	81
	0.110	80	
13	0.087	63	64
	0.090	65	

TABLE III

RECOVERY OF SMALL QUANTITIES OF BISMUTH FROM WATER SOLUTIONS CONTAINING HCl

Sample	*A (obs)*	*Bi Added (γ)*	*Bi Recovered (γ)*
1	0.083	10	8.6
2	0.098	10	10.2
3	0.410	50	43
4	0.446	50	47
5	0.895	100	94
6	0.895	100	94

To test the recovery at low levels of bismuth, solutions containing 10, 50, and 100 γ of bismuth were processed according to the procedure indicated for lead at pH 6.25 (the final volume in this case was 25 ml). The absorbance of these solutions was measured in 5 cm cells and referred to a calibration plot (Table I) to obtain the bismuth recovery. The results, indicated in Table III, show that good recovery even at low bismuth content is possible.

When the gathering step is carried out on lead samples it is necessary to make a preliminary separation of the bulk of the lead. The chloride separation was employed since lead sulfate reportedly occludes bismuth[26,23,15,5,16]. (The effect of fuming temperature on bismuth retention noted by ETHERIDGE[10] was not investigated.) Even though most of the lead is removed, the saturation value for lead chloride persists. Consequently, the bismuth recovery was studied in the presence of lead in a chloride medium. Seventy mg of lead (as the nitrate) and 300 γ of bismuth were added to 130 ml of water, 50 ml of $4M$ sodium chloride, 1.5 ml of nitric acid, and 10 ml of hydrochloric acid. The bismuth was collected as above. The bismuth recovery as a function of pH is tabulated in Table IV. The recovery is the same as for lead-free solutions.

TABLE IV

EFFECT OF PH ON BISMUTH RECOVERY FROM SOLUTIONS CONTAINING 70 mg OF LEAD

pH	*A (obs)*	*% Bi Recovered*
4	0.042	30
5	0.091	67
6	0.138	100
6.5	0.137	99
7	0.138	100
8	0.137	99
9	0.138	100
10	0.137	99
11	0.126	91
12	0.110	80

TABLE V

EFFECT OF PH ON BISMUTH RECOVERY FROM SOLUTIONS CONTAINING 350 mg OF LEAD

pH	*A (obs)*	*% Bi Recovered*
5.00	0.043	31
5.25	0.125	91
5.50	0.136	99
5.75	0.125	91
6.00	0.127	92
6.25	0.129	94
6.50	0.131	95
7.25	0.076	55

Addition of 350 mg of lead compresses the pH range over which satisfactory recoveries are possible as shown in Table V. The reduction in recovery at higher lead concentration and at higher pH values confirms the observation that lead sulfate occludes bismuth. Under these conditions more lead would be expected to precipitate with the bismuth. The elution treatment with sulfuric acid would yield lead sulfate and result in lower recoveries.

To simulate better the actual conditions under which the gathering step would be carried out when applied to lead samples, the effect of pH was studied on samples containing 300 γ of bismuth in a solution of 20 g of lead (as the nitrate) dissolved in 70 ml of water and 5 ml of nitric acid. This is similar to the composition of solutions obtained by dissolving 20 g of metallic lead in nitric acid. The samples were processed as in the procedure except that the pH at gathering was varied. Quantitative recovery of bismuth between pH 6.0 and 6.5 is shown by the data of Table VI. This is the identical range found for recovery on ferric hydroxide by BALLARD AND BALLARD[3]

TABLE VI

EFFECT OF PH ON BISMUTH RECOVERY FROM LEAD NITRATE SOLUTIONS WITH PRIOR REMOVAL OF LEAD WITH HCl

pH	*A (obs)*	*% Bi Recovered*
5.75	0.127	92
6.00	0.138	100
6.25	0.138	100
6.50	0.134	97
6.75	0.123	89

The recovery of 0-100 γ of bismuth from 20 g of lead using the above procedure and gathering at pH 6.25 is shown in Table VII. These data indicate that at least 10 γ of bismuth can be determined in 20 g of lead, and this corresponds to 0.00005% bismuth.

TABLE VII

RECOVERY OF SMALL QUANTITIES OF BISMUTH FROM LEAD NITRATE SOLUTIONS WITH PRIOR REMOVAL OF LEAD WITH HCl

Sample	*A (obs)*	*Bi Added (γ)*	*Bi Recovered (γ)*
1	0.012	0	1
	0.008	0	1
2	0.085	10	9
	0.090	10	9
3	0.240	20	25
	0.185	20	19
4	0.484	50	51
	0.475	50	50
5	0.600	70	63
	0.648	70	68
6	0.855	100	90
	0.924	100	97

The effect of antimony on bismuth recovery was estimated by determining the recovery of 300 γ of bismuth in the presence of 20 mg of antimony from solutions containing 20 g of lead. Under the conditions of the procedure the bismuth recovery was reduced to 90% when the antimony absorption was accounted for.

In samples containing up to 1 mg of bismuth it is possible to gather almost all the bismuth from 20 g of lead using the recommended procedure and an elution with 12.5 ml sulfuric acid. Specifically 0.93 mg was found when 1.0 mg was added. However, 50 ml of sulfuric acid are required to quantitatively elute 10 mg of bismuth. This quantity of bismuth can be gathered on the silica by the recommended procedure, and the use of a larger volume of acid is not serious since the eluate must be diluted to obtain a reasonable absorbance value. This wide range of bismuth content over which the procedure is applicable is valuable since 20 g lead samples containing 0.00005-0.05% bismuth can be analysed without danger of having to repeat the operations on a smaller sample.

An attempt was made to eliminate neutralization of the hydrochloric acid in the gathering step by substituting sodium chloride for the acid in the precipitation of lead chloride. One hundred ml of 4*M* sodium chloride were substituted for the 30 ml of acid. Samples containing 300 γ of bismuth, added to 20 g of lead as above, failed to give satisfactory bismuth recoveries. Further investigation showed that bismuth was lost during the gathering step since low recoveries were also obtained when the bismuth was added to the lead chloride filtrate. The lead content of these filtrates obtained from precipitation of 30 g of lead nitrate with sodium chloride was found to be 530 mg of lead by gravimetric analysis. However, the filtrates from hydrochloric acid precipitation were found to contain only 315 mg of lead. Attempts were made to raise the bismuth recovery in the presence of this increased quantity of lead. Addition of citrate in the gathering step prevented precipitation of basic lead salts, but the bismuth was also complexed and low recoveries were obtained. Prewashing the silica, after gathering, with hot 50% ammonium acetate to remove lead also removed bismuth, and the subsequent elution with sulfuric acid gave low recoveries. Sodium hydroxide at 0.1*M* concentration likewise failed to remove lead without removing bismuth. At 0.01*M* sodium hydroxide concentration no bismuth was washed off, but the recovery was not increased. Failure to increase the bismuth recovery resulted in adoption of hydrochloric acid as the lead chloride precipitation agent since the cleaner separation of lead is required for satisfactory gathering of bismuth.

The presence of fine particles of silica occasionally produces turbid solutions which are not suitable for photometry in 5 cm cells required at low bismuth levels. No difficulties due to turbidity were ever experienced when 50 ml of sulfuric acid were used to elute the bismuth and the absorbance was determined in 1 cm cells. Filter paper is not suitable for removing the fine silica since it reduces the color intensity of the bismuth iodide complex. However, a fine sintered glass filter was found to remove the turbidity without altering the absorbance.

The time required is one hour per determination when six samples are run simultaneously.

Results on commercial samples

Although the procedure has been tested with samples of pure lead to which known amounts of bismuth have been added, tests on commercial samples of lead of established bismuth content would be desirable. However, since such samples are not available, it is of interest to examine such materials which are near or below the concentration level indicated by other methods.

Lead samples obtained from equipment used in the manufacture of smokeless powder were analysed by the recommended procedure. These samples had been examined previously by the spectrographic technique and found to contain less than 0.0005% bismuth. Another sample was supplied by a manufacturer of storage batteries. This sample had been prepared by dilution of a sample of known high bismuth content with pure lead and designed to contain 0.0002% bismuth. Spectrographic analysis had shown the bismuth content to be in this range. The results for duplicate analyses of all the samples are given in Table VIII.

TABLE VIII

ANALYSIS OF LEAD SAMPLES FOR BISMUTH CONTENT

Sample	*A (obs)*	*Bismuth*	*Content*
—	—	(γ)	(%)
A	0.080	8	0.00004
	0.051	5	0.00003
B	0.399	42	0.00021
	0.371	38	0.00020
C	0.888	93	0.00047
	0.845	89	0.00045
R-14	0.052	5	0.00003
	0.042	4	0.00002
R-16	0.059	6	0.00003
	0.074	8	0.00004
R-20	0.142	15	0.00008
	0.154	16	0.00008
SOW 2	0.580	61	0.00031
	0.533	56	0.00028
HS 2	0.360	36	0.00018
	0.374	39	0.00020
H	0.544	57	0.00029
	0.544	57	0.00029

PROCEDURE FOR DETERMINATION OF TRACES OF BISMUTH IN COPPER

Apparatus and materials

The equipment and many reagents used are the same as for the lead analysis. Additional reagents are listed below.

Copper nitrate trihydrate, $Cu(NO_3)_2 \cdot 3H_2O$.
Ammonia
Ammonium chloride

Method

The following procedure is based in part on the one recommended by the Fiscal Policy Joint Committee of the (British) Brass, Copper, and Nickel Silver Industries[11].

Dissolve 2 g of drillings in 20 ml of 1:1 nitric acid in a 400 ml beaker (see Note 1 for treatment of any insoluble material). Add 100 ml of water followed by 5 g of ammonium chloride and adjust the pH to 9 by the addition of ammonia. Add 2.5 g of silica flour. (If the bismuth content does not exceed 100 γ, 1 g may be added. This allows somewhat easier manipulation.) Allow the solution to stand for 1 hour with intermittent agitation. Filter off the silica on a Gooch crucible prepared as above and wash 3 or 4 times with 1:5 ammonia to remove copper. Then wash 3 times with water. Elute the bismuth from the silica with 12.5 ml of hot 1:20 sulfuric acid as described in the lead analysis. Add 1 ml of 30% hypophosphorous acid and 0.375 g of potassium iodide to the eluate. Dilute to 25 ml and if the solution is turbid filter through a fine sintered glass filter. Measure the absorbance at 460 mμ to determine the bismuth content.

Note 1

Any metastannic acid or other insoluble material remaining after solution of the sample should be fused with potassium pyrosulfate, the melt leached with dilute sulfuric acid and the filtered solution added to the main solution. Addition of sulfate to the main solution would precipitate lead sulfate if much lead were present (10 mg or 0.5% will not precipitate) and it would be necessary to remove the precipitate before gathering the bismuth. This operation might be objectionable since some bismuth might be lost with the lead sulfate. However, the loss would not be expected to be so great as in the separation of bismuth from lead samples.

Discussion of the method for bismuth in copper

The separation of bismuth from copper is much easier than from lead. Conversion of copper to the soluble ammonia complex in the pH range where the bismuth can be collected (Table VI) provides an ideally simple separation and collection in one step. A pH of 9 was chosen because bismuth recovery is complete at this pH and the copper is readily solubilized. Recovery of 300 γ of bismuth was complete at pH 9 from copper solutions containing 2 g of copper (added as $Cu(NO_3)_2 \cdot 3H_2O$) in 120 ml of water and 2 ml of nitric acid (Table IX).

TABLE IX

RECOVERY OF BISMUTH FROM COPPER NITRATE

Sample	*A (obs)*	*Bi Recovered %*
Blank	0.000	0
1	0.136	98
2	0.140	100

Zinc does not interfere with bismuth recovery. To simulate a dissolved brass sample a solution containing 1.6 g of copper plus 0.4 g of zinc (equivalent to 20% Zn on a 2 g sample basis) and 300 γ of bismuth was prepared as above and processed. (The copper was added as $Cu(NO_3)_2 \cdot 3H_2O$ and the zinc as $Zn(NO_3)_2 \cdot 6H_2O$.) No loss of bismuth was noted, and therefore the procedure may be applied to brass samples.

Iron in amounts of 0.5% (based on a 2 g sample again) also has no effect on the bismuth recovery. However, a similar amount of lead reduced the recovery to about 90% (Table X). This also appears to be due to occlusion of bismuth by lead sulfate.

The recovery of 0-100 γ of bismuth from solutions containing 2 g of copper (as the nitrate) is shown in Table XI. A sample containing 10 mg of bismuth showed a 98% recovery when the final solution was diluted to obtain a reasonable absorbance.

These results indicate that as little as 10 γ or as much as 10 mg of bismuth can be determined in copper. This corresponds to a range of 0.0005 to 0.5% bismuth if a 2 g sample is used. This wide range eliminates the possibility of having to repeat an analysis on a different size sample.

TABLE X

EFFECT OF ZINC, IRON, AND LEAD ON BISMUTH RECOVERY FROM COPPER

Sample	*Foreign material added* (*% based on 2 g sample*)	*A* (*obs*)	*Bismuth Recovery* (%)
1	Zn, 0.4 g (20%)	0.142	103
		0.138	100
2	Fe, 10 mg (0.5%)	0.142	103
		0.138	100
3	Pb, 10 mg (0.5%)	0.127	92
		0.125	91

TABLE XI

RECOVERY OF SMALL QUANTITIES OF BISMUTH FROM 2 g OF COPPER

Sample —	*A* (*obs*) —	*Bi Added* (γ)	*Bi Recovered* (γ)
1	0.000	0	0
	0.000	0	0
2	0.100	10	10
	0.095	10	10
3	0.184	20	19
	0.199	20	19
4	0.355	40	37
	0.391	40	40
5	0.649	70	67
	0.664	70	69
6	0.951	100	100
	0.947	100	99

The use of silica as a gathering agent for bismuth offers several advantages over other methods. Dithizone has been used to preconcentrate bismuth[1,10,13], but in the presence of lead the procedure is very tedious and there is some doubt that bismuth is completely extracted[28]. The procedure is also very long since the chloroform extracts must be evaporated and re-extracted into aqueous medium for destruction of organic matter with hydrogen peroxide[10]. Extraction of bismuth with cupferron at pH 1[16] is not entirely satisfactory since it is somewhat difficult to adjust the pH accurately, and quantitative bismuth recovery is not always obtained. If ferric hydroxide is used to collect bismuth from copper[3,4,20,25,26,29,31] long standing and reprecipitation are required. In addition the iron tends to oxidize iodide and forms a color with thiocyanate thereby interfering with these colorimetric methods for bismuth evaluation. The use of aluminum hydroxide[19] and manganese dioxide[6,14,24,35] both require double precipitation for complete bismuth recovery. Deposition of bismuth on copper[17] results in only 80-90% recovery. Therefore, the use of silica as a gathering agent is advantageous because it allows rapid and quantitative gathering of bismuth in one step without reprecipitation. Furthermore, its use places no restrictions on the selection of the method used for final bismuth estimation.

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SUMMARY

The presence of bismuth gives rise to unfavorable properties in lead and copper and procedures for its determination in very small quantities are desirable.

A method of analysis has been developed for lead materials in which most of the lead is removed from a 20 g sample as the chloride and the bismuth in the filtrate is collected at pH 6.00-6.25 on silica flour. The bismuth is eluted with dilute sulfuric acid and is determined colorimetrically as the iodide. Copper samples do not require a preliminary removal of the copper, since it can be converted to the soluble ammonia complex at the stage where the bismuth is collected on the silica flour. Quantities of bismuth of the order of 0.00005% in lead and 0.0005% in copper are determinable. The use of silica as a gathering agent has distinct advantages over previously used materials.

RÉSUMÉ

La présence de bismuth altère les propriétés du plomb et du cuivre; il est nécessaire d'avoir à sa disposition des méthodes permettant de doser de très faibles quantités de cet élément. Une méthode d'analyse est proposée pour des échantillons de plomb; la plus grosse partie du plomb est éliminée comme chlorure; le bismuth dans le filtrat est collecté sur de la poudre de silice au pH 6.00 - 6.25; il est ensuite dissous dans l'acide sulfurique dilué et dosé colorimétriquement comme iodure. Dans le cas des échantillons de cuivre, il n'est pas nécessaire d'éliminer cet élément, puisqu'il peut être transformé en complexe amminé soluble. Des quantités de bismuth de l'ordre de 0.00005 % dans le plomb et de 0.0005% dans le cuivre peuvent être dosées. L'emploi de la silice comme collecteur présente des avantages sur les substances déjà utilisées.

ZUSAMMENFASSUNG

Die Anwesenheit von Wismuth ändert die Eigenschaften von Blei und Kupfer. Es ist notwendig Methoden zur Verfügung zu haben, welche erlauben sehr schwache Quantitäten dieses Elementes zu bestimmen. Es wird eine Analysenmethode für Blei vorgeschlagen, wobei der grösste Anteil dieses Elementes als Chlorid eliminiert wird. Das Wismuth im Filtrat wird auf Silizium in Pulverform bei pH 6.00 - 6.25 angesammelt. Es wird darauf in verdünnter Schwefelsäure aufgelöst und kolorimetrisch als Jodid bestimmt. Im Falle von Kupfer ist es nicht nötig dieses Element zu eliminieren, weil es in einen löslichen Amminkomplex überführt werden kann. Wismuthmengen in der Grössenordnung von 0.00005% in Blei und von 0.0005% in Kupfer können bestimmt werden. Die Verwendung von Silizium als Kollektor weist gegenüber schon gebrauchten Substanzen Vorteile auf.

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SOME ANALYTICAL APPLICATIONS OF DIFFUSE REFLECTANCE MEASUREMENTS*

by

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The measurement of diffuse reflectance has been made a rather simple procedure by the commercial availability of a diffuse reflectance attachment for Beckman spectrophotometers.[1] The spectral properties of opaque materials can be measured by means of this unit. The light scattered from the sample is gathered by a ring shaped ellipsoidal mirror which casts that light onto the phototube detector. Only diffusely scattered light is collected by this mirror. Typical applications reported for this type of measurement include the determination of dirt on cloth[2] and the study of sodium-tungsten bronzes[3]. An evaluation of the method has recently been published[4], with particular emphasis upon dyed samples of cloth and yarn and synthetic mixtures of pigments.

The present study is in two parts. Part one deals with the study of colored materials adsorbed onto strips of filter paper. Part two involves measurements upon powdered solid substances.

Colored materials adsorbed onto filter paper

The experimental steps used in this part of the study include the following: standard solutions of the colored substance were prepared; a circle of dry filter paper was dipped into each solution; the paper was removed and allowed to dry; then its reflectance properties were measured against a blank circle of the paper as a reference standard. From the results of these measurements, the possible analytical usefulness of the procedure was determined.

The nature of the colored substance is of interest. In some cases, the reflectance spectrum is the same as the transmission spectrum of the solution, while with other substances the two differ. In Fig. 1 are shown spectra for transmission through a solution of malachite green and for reflectance from the dried strip of filter paper after insertion in the solution. Both spectra are essentially alike except for a moderate difference in absorption band widths, so the substance responsible for the spectral characteristics must be very similar in both conditions. The two corresponding spectra for copper ammine are shown in Fig. 2. There is a definite shift in absorption from the wavelength corresponding to the tetrammine in solution to, probably, some intermediate ammoniated salt in the dry state.

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* Contribution No. 684 from the Chemistry Department of Indiana University.

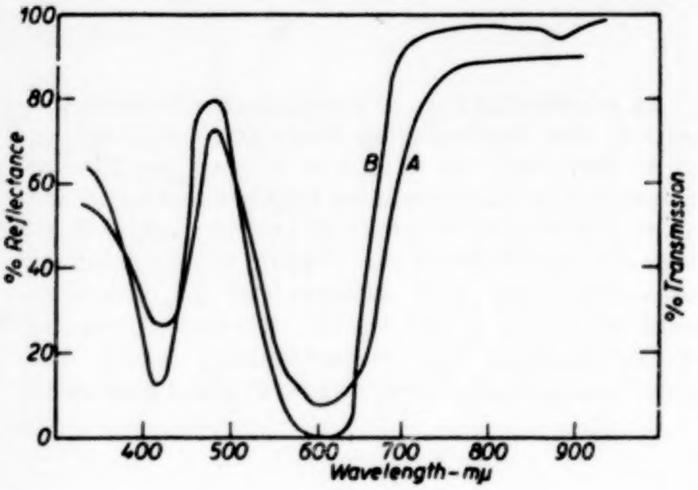

Fig. 1. Spectra for malachite green: A. diffuse reflectance from paper strip; B. direct transmission through solution.

Because of the possible chemical alteration of the colored substance upon drying, a standard drying time and procedure must be adopted. Even in systems such as that represented by Fig. 2, reproducible results can be achieved when the drying time prior to measurement is held reasonably constant.

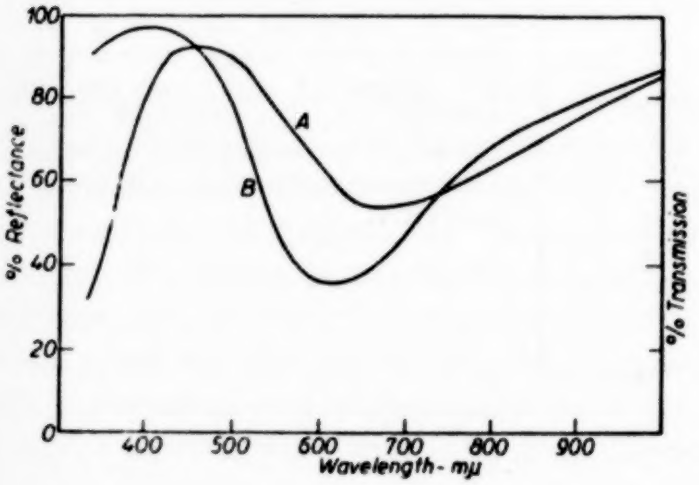

Fig. 2. Spectra for copper ammine: A. diffuse reflectance from paper strip; B. direct transmission through solution.

The type of paper used was found to influence the reflectance properties, both of the blank paper and of the paper after dipping into the colored solution and drying. A high porosity, highly reflecting paper, Whatman No. 2, was found very satisfactory, although some other papers can also be used.

The duration of time during which the paper strip is immersed in the colored solution was found to be of no significance. With one solution and one type of paper, immersion from one second to one hour resulted, after drying, in the same reflectance values.

Four colored systems were investigated by this procedure for possibly useful analytical application. For each system a series of standard solutions was prepared, paper circles were inserted and allowed to dry, and the diffuse reflectance of each was measured at wavelength corresponding to a minimum in the reflectance spectrum. The data were plotted in a method analogous to the conventional Ringbom plots for direct spectrophotometric work in order to ascertain the concentration range of usefulness. The useful concentration range was taken as that corresponding to 100-%R values of 20 to 80; the plots were approximately linear throughout this range. (%R is the observed % reflectance.)

Copper ammine

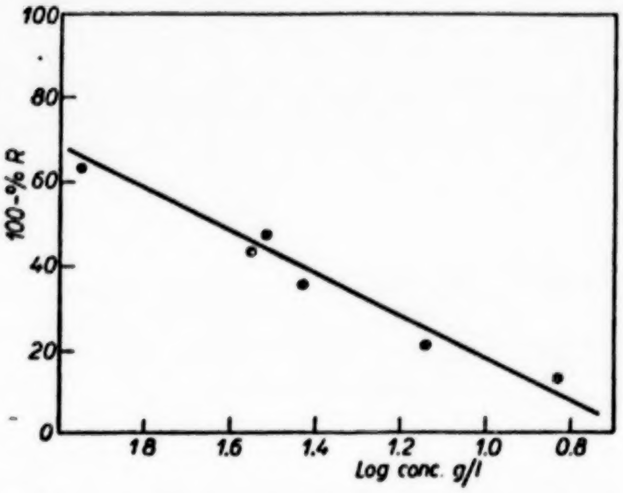

Fig. 3. Copper ammine calibration plot.

As revealed in Fig. 3, useful data are obtained within the approximate concentration range of 12 to well over 100 grams of copper per liter of solution. The slope remains nearly constant down to even lower concentrations and the upper limit was not investigated thoroughly, so this estimate of useful range is a conservative one. The concentration range for useful determinations by direct transmission measurements upon the solutions is much lower and somewhat narrower.

Iron thiocyanate

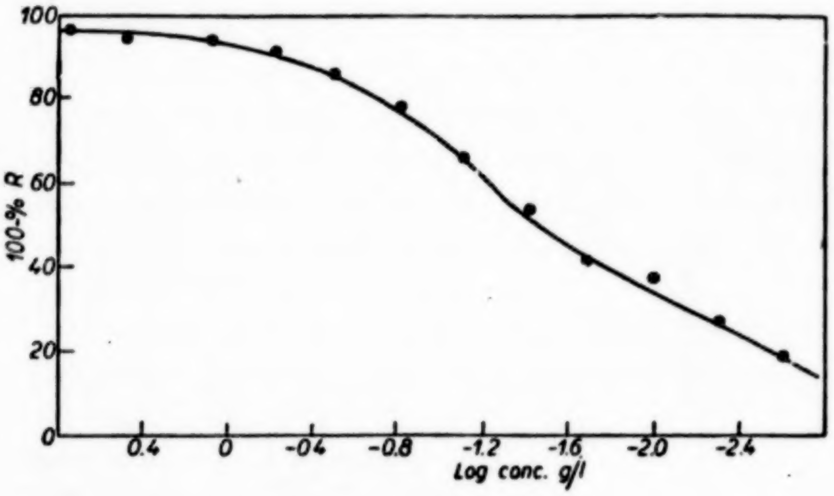

Fig. 4. Iron thiocyanate calibration plot.

As revealed in Fig. 4, the reflectance measurements provide useful analytical data over the concentration range of 0.003 to 0.2 grams of iron per liter of solution. The concentration range for useful determinations by transmission measurements is somewhat narrower.

Malachite green

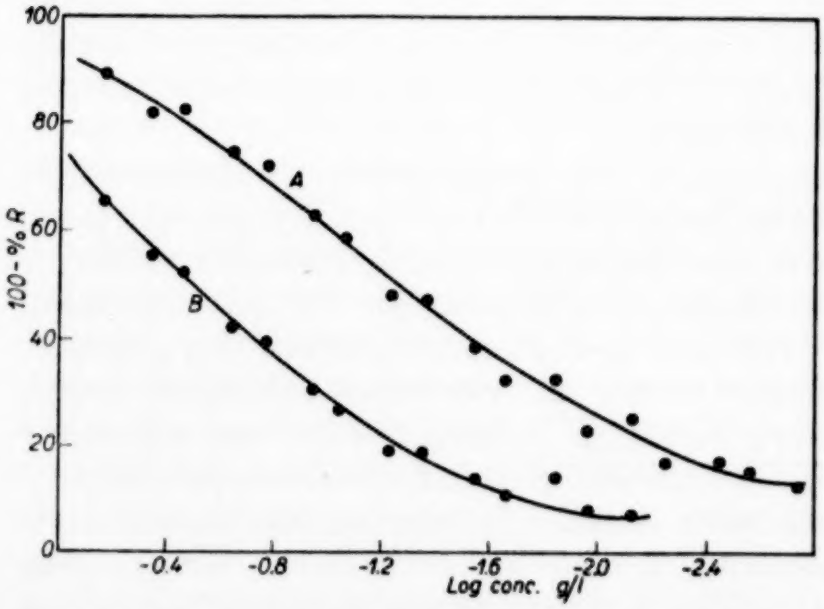

Fig. 5. Malachite green calibration plot: A. at 620 mμ; B. at 420 mμ.

The data of Fig. 5 reveal analytically useful data within the approximate concentration range of 0.008 to 0.4 grams solute per liter of solution at a wavelength of 620 millimicrons and a range of about 0.06 to well over 1.0 gram per liter at the 420 millimicron wavelength. The correspondingly useful range for direct transmission is somewhat less but overlapping.

References p. 593.

Congo red

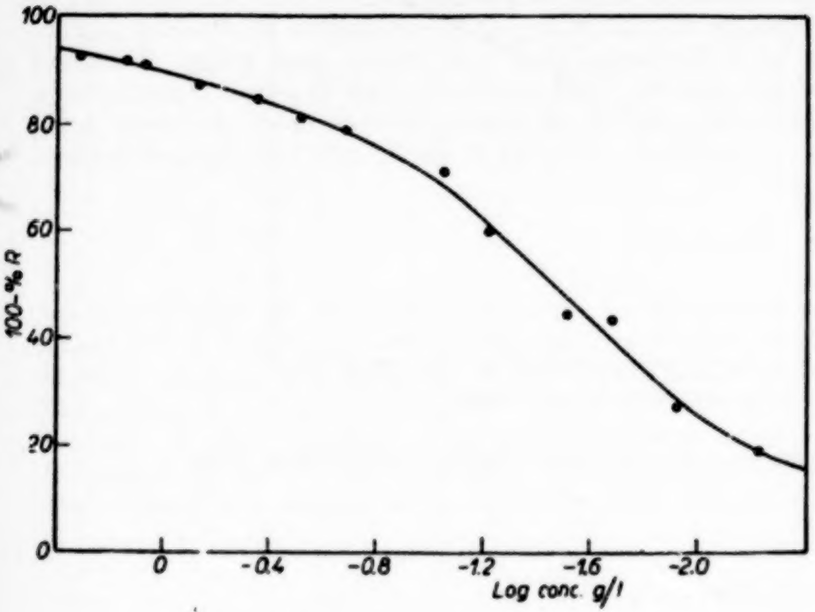

Fig. 6. Congo red calibration plot.

In Fig. 6 are shown data for the reflectance determination of congo red. The useful concentration range extends from about 0.006 to about 0.25 grams of solute per liter of solution.

In all of these stated ranges, it must be recognized that they are based upon an arbitrary choice of 20 and 80 as the limiting values of 100 - % reflectance. Most of the plots are quite linear over even wider ranges, so these ranges are all listed quite conservatively. In general, the correspondingly ascertained useful ranges for determination by direct transmission measurement upon the solutions are somewhat narrower and at lower concentrations. So it appears that there is a distinctively useful place for the use of this reflectance technique in analytical chemistry. In both reflectance and transmission methods, the useful range may be varied by choice of various wavelengths for measurement.

Powdered solid substances

The colored, powdered substance to be measured was mixed with U.S.P. magnesium carbonate and pressed by hand into an aluminium planchet (of the type commonly used in radiochemistry work). The reflectance properties were measured against a block of magnesium carbonate as a reference standard. It was found possible to reproduce a surface so that reflectance measurements were in agreement within one-half of one percent with reasonable care to insure complete mixing.

As with the colored strips of filter paper described above, several types of data plot are possible. The *100 - % Reflectance* versus *log wt % of colored substance* is one of several convenient and useful forms. Data are shown in Figs. 7, 8 and 9 for representative substances. There is appreciable scatter due to variability in preparing and mounting the samples into the planchets, but the consistency is adequate for reasonably quantitative work in each of these systems.

The study of mixtures containing more than one colored component is quite complex. No analytically useful means of interpreting reflectance measurements upon such mixtures was found in the present study.

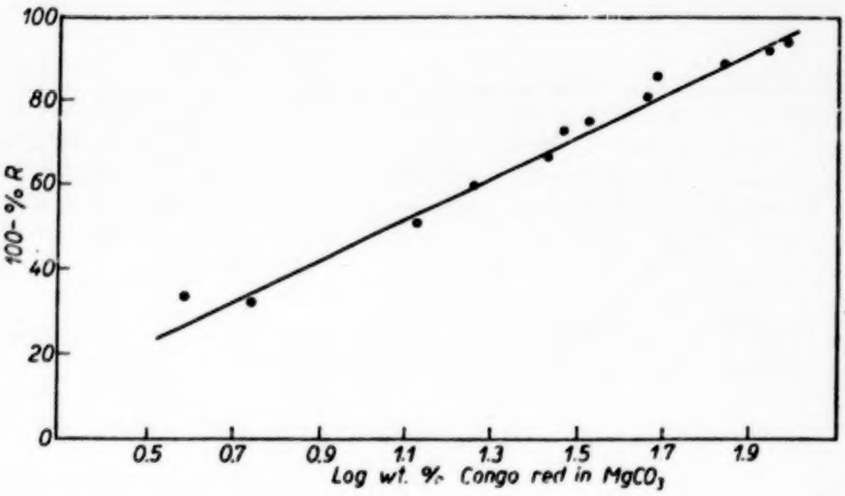

Fig. 7. Powdered mixture of congo red and $MgCO_3$, calibration plot.

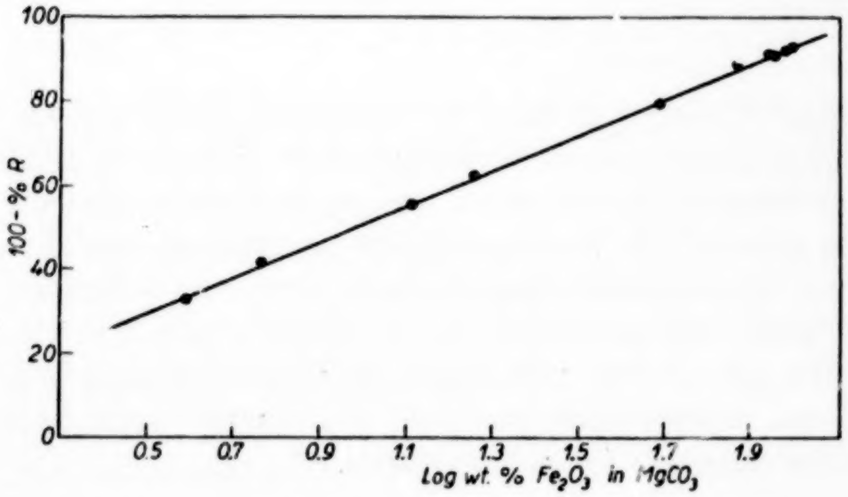

Fig. 8. Powdered mixture of naphthol yellow S and $MgCO_3$, calibration plot.

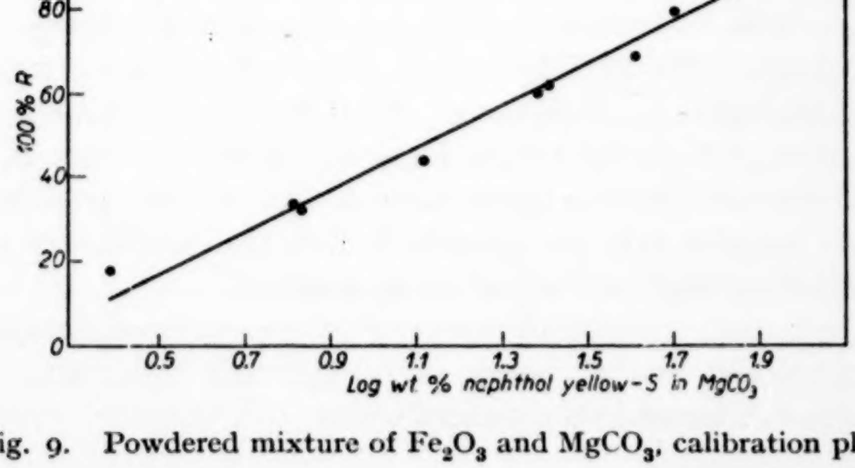

Fig. 9. Powdered mixture of Fe_2O_3 and $MgCO_3$, calibration plot.

References p. 593.

SUMMARY

The similarities and dissimilarities between diffuse reflectance and direct transmission properties have been indicated. Data are given for solutions of copper ammine, iron thiocyanate, malachite green and congo red, each adsorbed onto strips of filter paper and dried. The approximate range of each for analytical use was determined. Results of measurements upon solid, powdered mixtures are presented. Quantitative procedures are possible for determining the composition of mixtures of which only one component is colored.

RÉSUMÉ

Les analogies et les différences entre les propriétés de la réflectance diffuse et celles de la transmission directe ont été examinées. Des données sont décrites pour des solutions de cuivre-ammine, de thiocyanate de fer, de vert de malachite et de rouge congo, chacun de ces composés étant absorbé sur des bandes de papier filtre et séché. Pour chacun de ces composés le domaine de concentration utile pour l'application analytique a été déterminé. Les résultats obtenus avec des mélanges solides pulvérisés sont donnés. Il est possible de déterminer quantitativement la composition de mélanges dans lesquels seulement un des constituants est coloré.

ZUSAMMENFASSUNG

Die Ähnlichkeiten und die Verschiedenheiten zwischen den Eigenschaften der diffusen Reflektanz und dieser der direkten Durchlässigkeit wurden untersucht. Es werden Angaben gemacht für Lösungen von Kupferammin, Eisenthiocyanat, Malachitgrün und Kongorot, welche auf Filterpapierstreifen absorbiert und getrocknet worden waren. Für jede dieser Verbindungen wurde das für analytische Anwendung nützliche Konzentrationsgebiet bestimmt. Resultate welche mit festen pulverisierten Mischungen erhalten wurden, sind angegeben. Es ist möglich die Zusammensetzung der Mischungen, in welchen nur ein Bestandteil gefärbt ist, quantitativ zu bestimmen.

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Received May 6th, 1955

THE FOOD DIVISION OF THE INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

COMMISSION FOR DETERMINATION OF TRACE ELEMENTS IN FOOD

REPORT ON ACTIVITIES 1954/1955

Members of the Commission are:
Prof. R. **Cultrera**, *Parma*
Prof. Ir. A. R. **Deschreider**, *Brussels*
Prof. Dr. W. **Diemair**, *Frankfurt am Main*
Prof. Dr. J. F. **Reith**, *Utrecht* (Chairman)
Dr. G. **Taylor**, *London*
Dr. L. **Truffert**, *Paris*
Dr. H. J. **Wichmann**, *Rugby, Tennessee*, (U.S.A.)

The Commission agreed on several general principles:

The Commission has to propose methods for furthering international commerce. It is hoped that the I.U.P.A.C. methods will be mentioned in commercial contracts. Since the methods are likely to be used in cases of arbitration, they must be specific, give reproducible results; simplicity is a less important requirement. If anybody wants a "Shortcut" method, he has to compose it on his own responsibility.

The methods must contain all details that may have influence on the results.

When used in arbitration, no changes in the method are allowed. If an improvement in the method is wanted, it may be proposed to the Commission.

The Commission does not intend to compose new methods, but it may experimentally study details. Collaborative analyses in the same samples are important.

Emission-spectrographical methods do not seem fit for the purpose. In some countries the polarograph generally is not available in official and industrial laboratories. Methods based on the use of organic reagents are preferred by the Commission. Some trace elements (*e.g.* tin), however, cannot be specifically determined with an organic reagent, in which case a polarographic or other method must be chosen.

Before the Commission chooses a method for the determination of a trace element, a member of the Commission will compose a review on literature available on the methods for that element. The other members will send him all references on the subject they possess; he himself will consult journals and abstracts to be sure of complete documentation. He will collect reprints or photocopies of the articles. He will write a critical review and propose a method to the Commission.

The following members of the Commission have undertaken to study specific trace elements: Dr. **Wichmann**, Lead; Prof. **Deschreider**, Tin; Prof. **Reith**, Mercury; Prof. **Diemair**, Zinc.

The "wet destruction" of organic materials by means of nitric and sulfuric acids seems safe for most trace elements. Dry ashing of organic materials often causes losses, f.i. of mercury, arsenic and copper. There is evidence that no lead is lost in careful incineration at temperatures below 500° C.

Precipitates can absorb metals and cause low results. This point will experimentally be studied by the Commission.

The members of the Commission principally agreed with a draft of a carbamate-versenate-method for copper. Collaborative analysis of samples according to that method are not yet finished.

The discussions on a method for lead are proceeding.

The determination of lead with dithizone according to **Snyder** and the reversion method with dithizone according to **Irving and Butler** are studied.

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BOOK REVIEWS

Qualitative Organic Analysis and Scientific Method, by A. MC GOOKIN, Chapman and Hall Ltd., London, 1955, 155 + vii pages, no figures, price 15/-d.

This work was compiled primarily for junior students in Universities and Technical Colleges, but the author's claim that it is sufficiently comprehensive to be of use to more advanced students of organic chemistry and biochemistry is, in the reviewer's opinion, amply justified.

The scheme of analysis is founded on the principle that qualitative organic analysis is the most important means of instilling the principles of scientific method into the minds of students of chemistry. Throughout the book, emphasis is laid on the three essentials of the methods of science: experiment, observation, inference. The result is a most refreshing approach to the subject and the book is much enlivened by apt quotations from others, including detective fiction. A valuable feature is that the student is encouraged to be clear-headed and critical and not to jump to hasty and incorrect conclusions.

The book covers a wide and representative range of substances, both aliphatic and aromatic. It is well produced and has a comprehensive index.

N. STRAFFORD (Manchester)

Gmelin's Handbuch der Anorganischen Chemie, 8. Edition, Gmelin-Institut, Verlag Chemie GMBH, Weinheim/Bergstrasse, 1955.

Nous sommes heureux d'annoncer à nos lecteurs la parution de trois nouvelles publications du remarquable ouvrage de chimie minérale. Ce sont:

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